Destructive Analysis Techniques for Safeguards

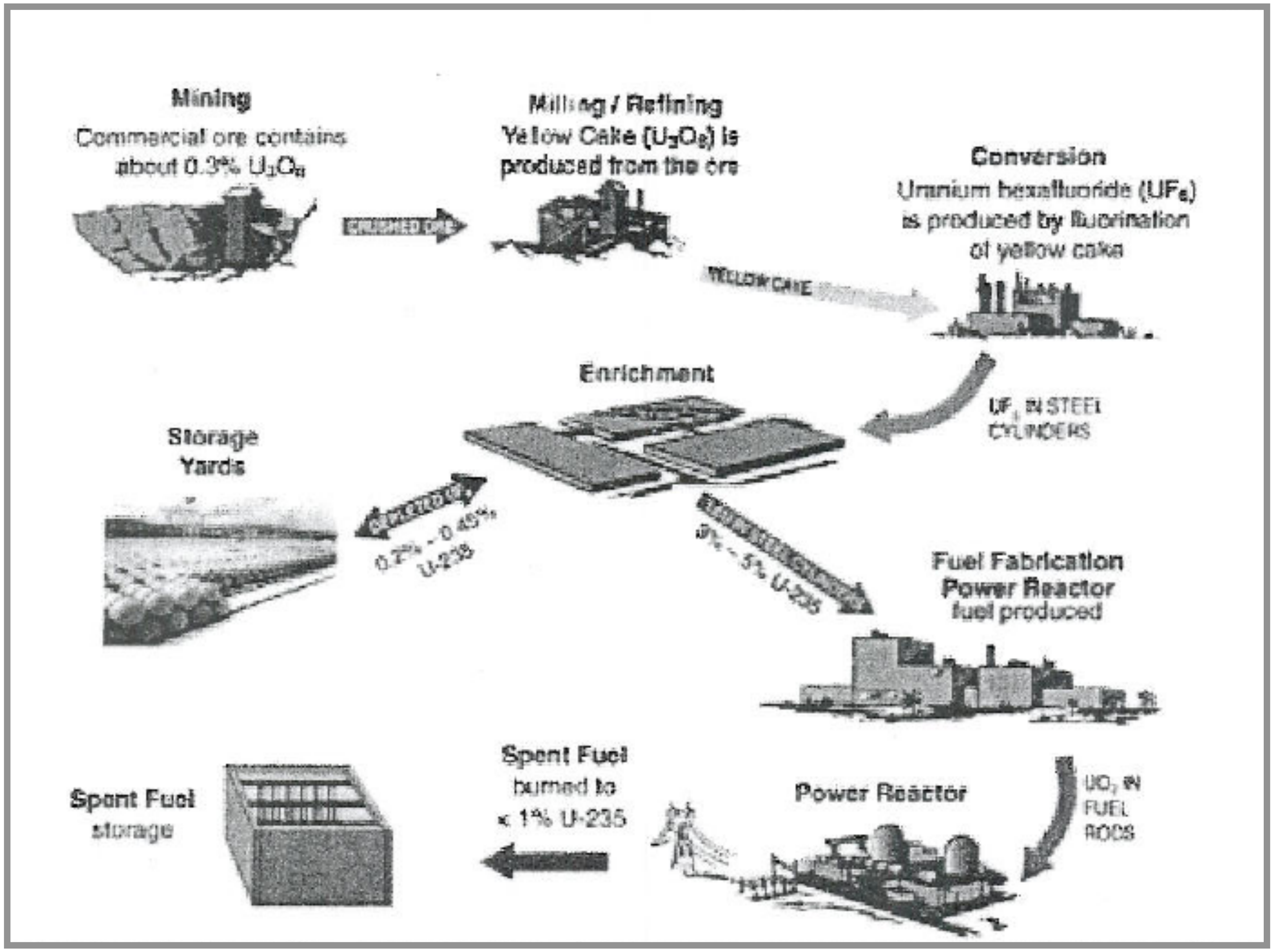
Stephen LaMont, Robert Steiner, Lav Tandon, and Paul Mendoza

15 June 2009

Outline

- Destructive Analysis
  - Definitions, Examples, Advantages / Disadvantages
- DA for traditional bulk SNM safeguards
  - U and Pu Assay methods
  - U and Pu Isotopic analysis methods
  - Elemental analysis / trace analysis methods for SNM characterization
- DA for environmental safeguards
  - NWAL program
  - Sample analysis
  - Analytical challenges
  - Quality assurance
- Summary

Uranium Fuel Cycle



Destructive Analysis

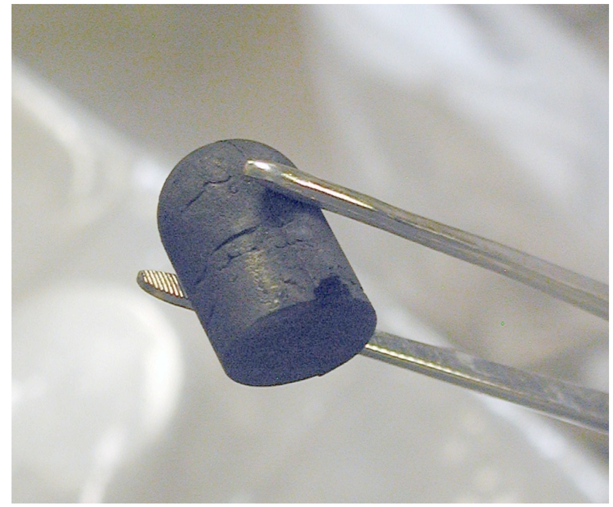
- Quantitative methods for determining elemental composition, elemental assay, or isotopic composition of a sample
- All or part of the sample is consumed in analysis
  - Sample cannot be recovered (eg. it is volatilized)
- Sample is irreversibly altered
  - Dissolved
  - Radiochemically purified
- Does not necessarily mean important sample attributes are destroyed
  - Analyte separated from matrix, but preserved

Examples of DA Techniques

- Elemental assay methods
  - Titration
- Elemental composition methods
  - Atomic emission spectroscopy
  - Mass spectrometry
- Isotopic analysis methods
  - Mass spectrometry
  - Alpha spectrometry
  - Radiochemical gamma-ray spectrometry
  - Radiochemical beta or liquid scintillation counting

Destructive Analysis for Safeguards

- Traditional Safeguards
  - Special Nuclear Material Accountability
  - Assay, isotopic, and impurity measurements critical for accurate accounting of SNM



- Environmental Safeguards
  - Swipe sampling in safeguarded facilities
  - Isotopic and assay measurements
  - Verification of facility declared operations
  - Detection of undeclared operations

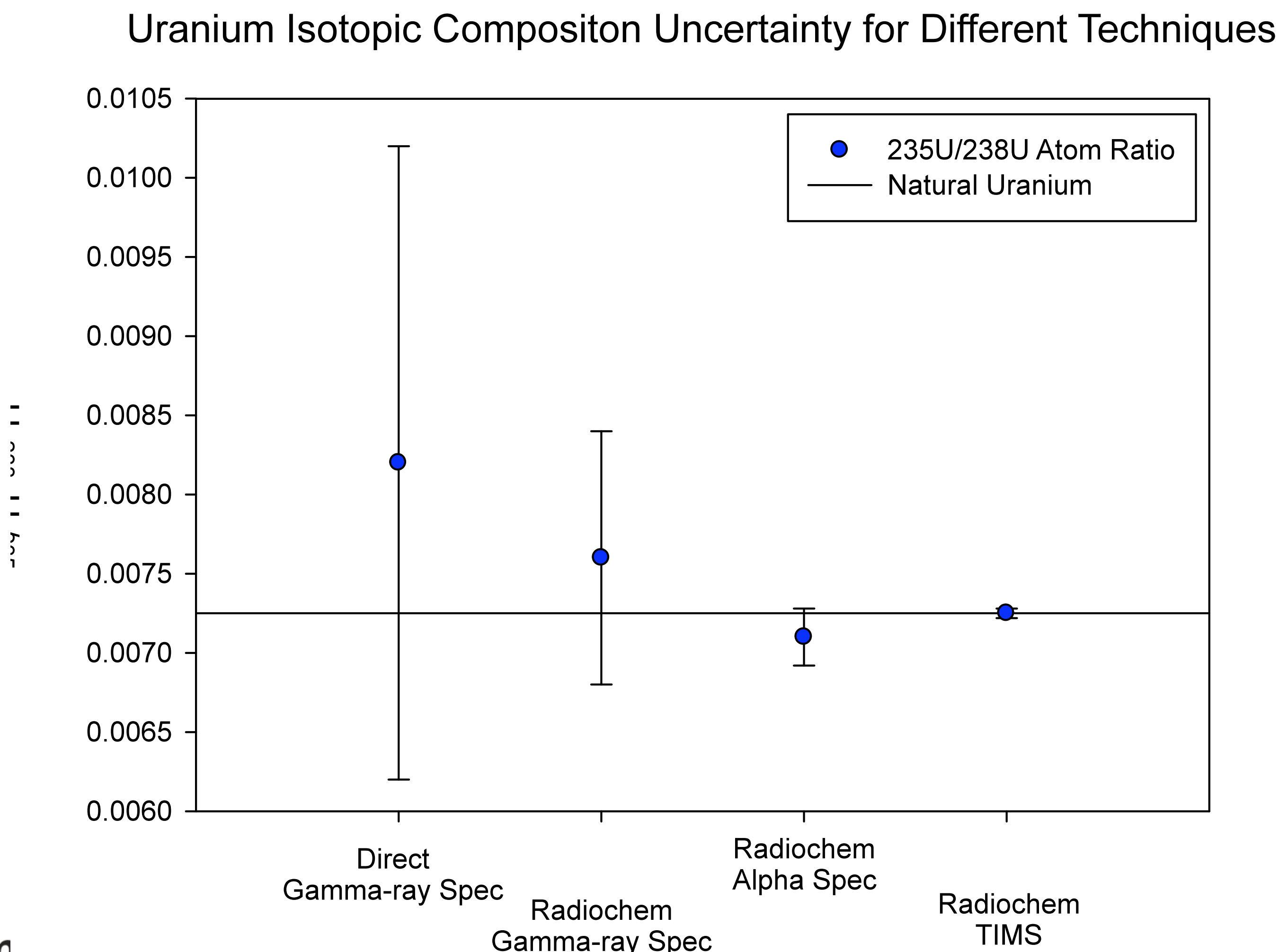
Glovebox

Advantages of Destructive Analysis

- Precision of DA techniques is usually much better than NDA methods
  - Effect of matrix can be eliminated or corrected

- Detection limits of DA techniques are usually lower than NDA methods
  - Eliminates background from matrix
  - Techniques are generally much more sensitive because of detection method (eg. atom counting vs. activity counting)

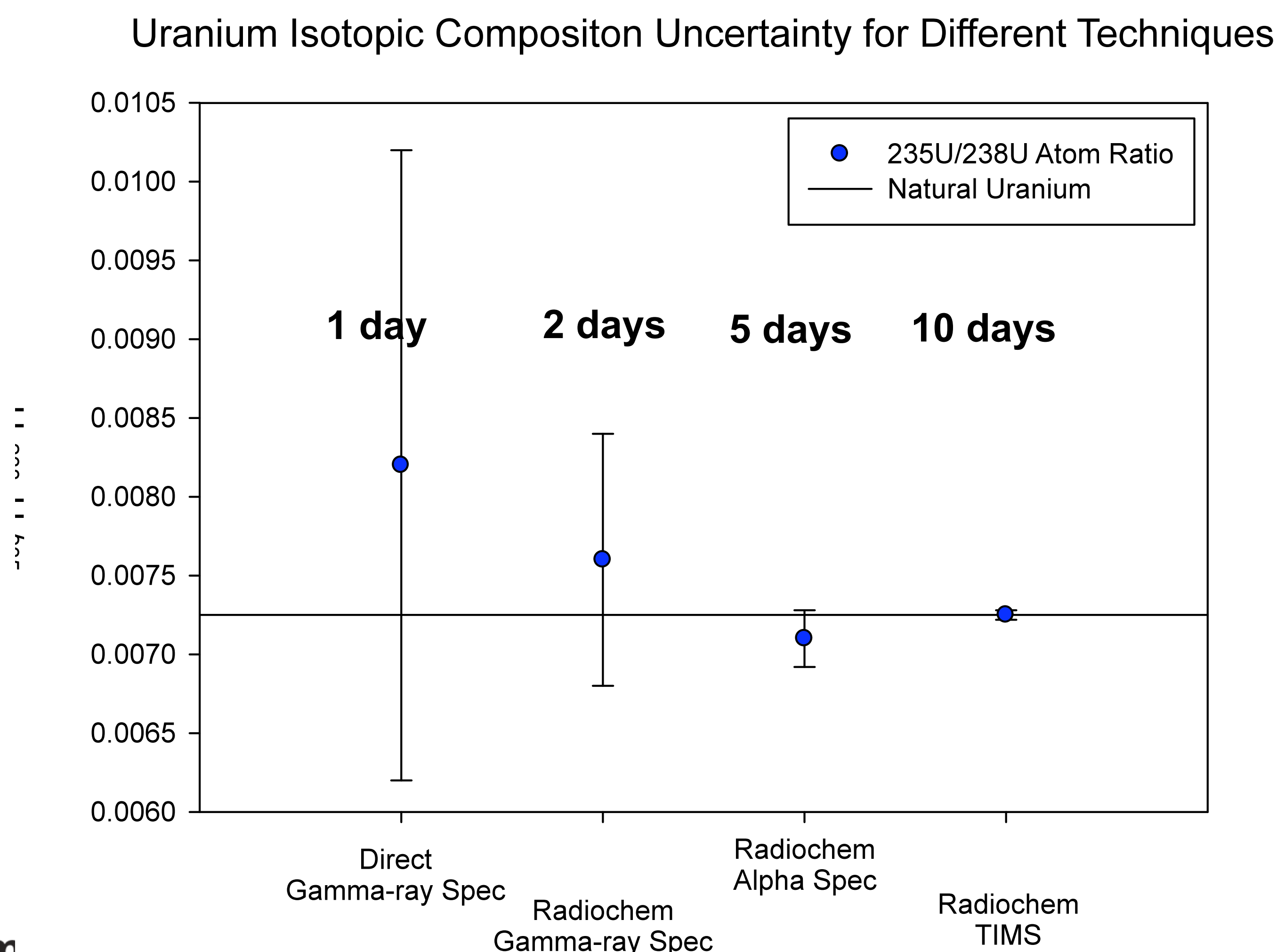
Comparison of Precision for NDA and DA Methods



Disadvantages of Destructive Analysis

- Typically much more labor intensive than NDA techniques
  - Sample preparation can take days to complete
- Opportunities to induce problems
  - Cross-contamination of samples
  - Contamination from previous facility operations
- More expensive than many NDA techniques
  - Instruments and supporting facilities are very expensive to build and maintain

Precision and Timeline for NDA and DA Methods



Dynamic Range of LANL Facilities (Plutonium)

TA-55 → **CMR** → **RC-1** → **RC-45**

10^3 g Pu → **10^{-6} g Pu** → **10^{-15} g Pu**

Weapons

Waste Characterization

Forensics

MPC&A / Safeguards

Environmental Measurements

Environmental Safeguards

Titration

Neutron Counting

ICP-MS

Calorimetry

Gamma-ray Spec

Alpha Spec

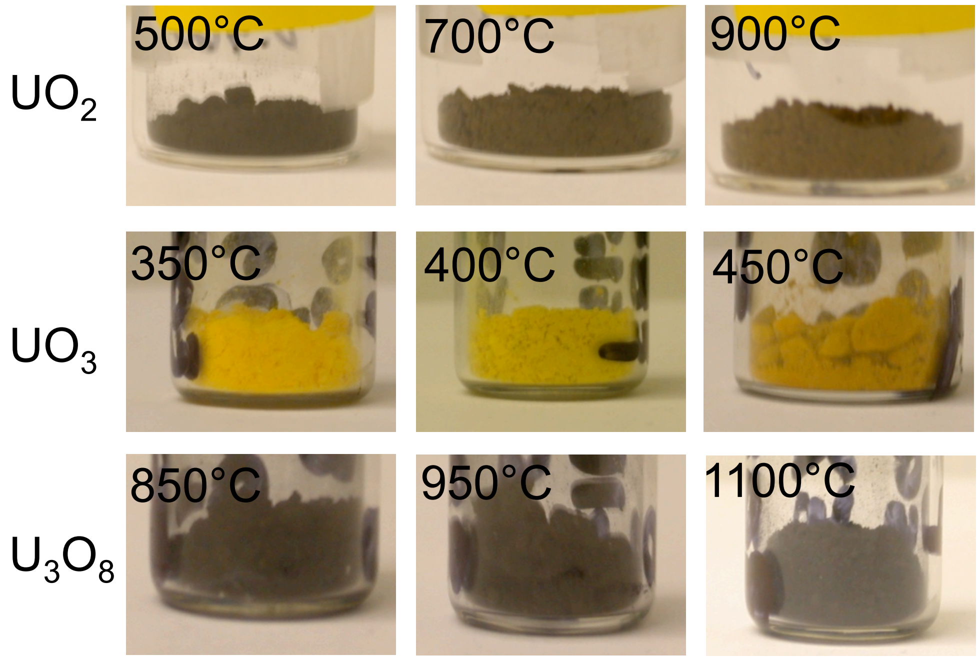
TIMS

← **Pu Assay and Isotope Ratios** →

Traditional Safeguards DA Measurements

- Uranium and Plutonium Accountability
- Large (mg – g) quantities used to ensure highest measurement precision (~0.5% or better)
- Assay
  - Titration or Isotope Dilution Mass Spectrometry
- Isotopic Analysis
  - Mass spectrometry or (rarely) alpha spectrometry
- Impurity Analysis
  - Atomic emission spectrometry
  - Inductively-coupled plasma mass spectrometry

Properties of Uranium Materials



- **Unique Properties**
- Color
- Texture
- **Uranium assay**

Redox or Electrometric Titrimetry—Davies and Gray Uranium Assay

- Used for a wide range of U materials including metal, oxides, nitrides, and moderately concentrated scrap solutions
- U(VI) is reduced to U(IV) by Fe(II) in H_3PO_4 and then titrated with $K_2Cr_2O_7$ to a potentiometric endpoint

$$\text{U(VI)} + \text{Fe(II)} \xrightarrow{\text{acid solution}} \text{U(IV)} + 2\text{Fe(III)}$$

$$\text{U(IV)} + \text{Cr(VI)} \xrightarrow{\text{catalyst}} \text{U(VI)} + \text{Cr(III)}$$

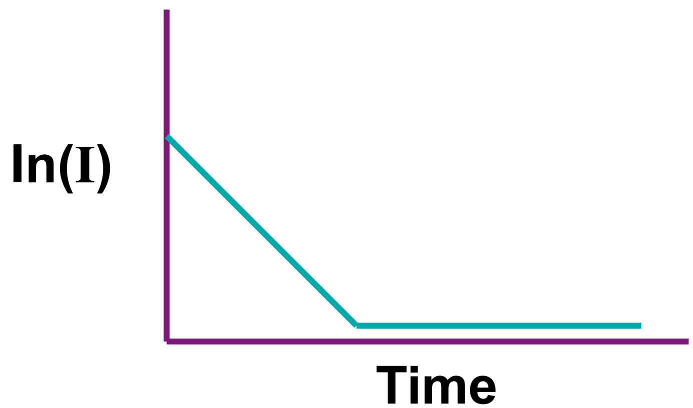
Redox or Electrometric Titrimetry—Davies and Gray Uranium Assay

- Minimal interference by ions typically present in U and U/Pu materials
- Metal samples are typically 300 – 500 mg
- Typically precision is ~0.05%, bias ~0.03 - 0.05%

Coulometric Plutonium Assay Titration

Used for a wide range of materials including metals, oxides, salts and solutions (~90% of the Pu samples analyzed at LANL)

$$Pu(III) \xrightarrow[0.5\ M\ H_2SO_4]{} Pu(IV)$$



Coulometric Plutonium Assay Titration

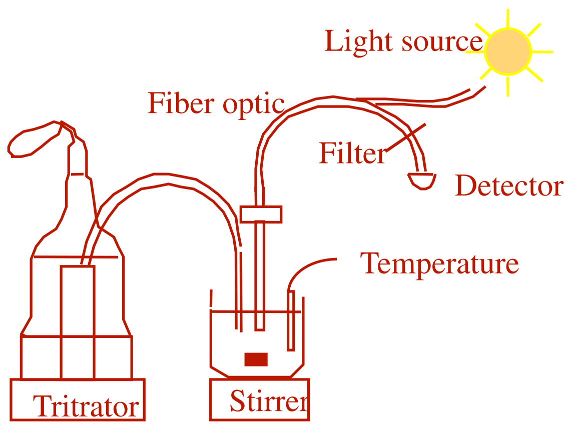
- Interferences include
  - Impurities that oxidize or reduce at 0.670 V (e.g., Fe)
  - Anions that complex Pu(III) or Pu(IV) and shift the potential of the Pu(III)/(IV) couple (e.g., phosphate, phosphite)
  - Components that adsorb onto the Pt working electrode and decrease its electrometric efficiency (e.g., organics, metallic ions —Zr(IV), Hf(IV), Ta(V), and Nb(V)—and elements including Ag, Au, Pd, Pt, Rh, and Ru
- Experienced chemist required
- Amount of Pu determined in an analysis is 5 – 7 mg
- Precision range ~0.08%

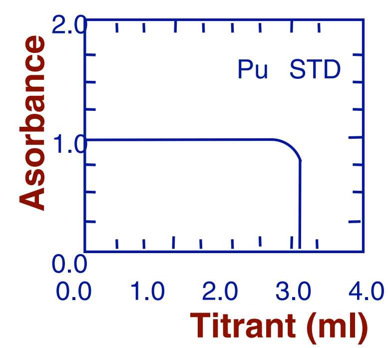
Ceric Titration for Plutonium Assay

- Used for assay of high purity Pu

$$Ce(IV) + Pu(III) \xrightarrow[(HCl/H_2SO_4)]{} Pu(IV)$$

Photometric endpoint is the color change of ferrion





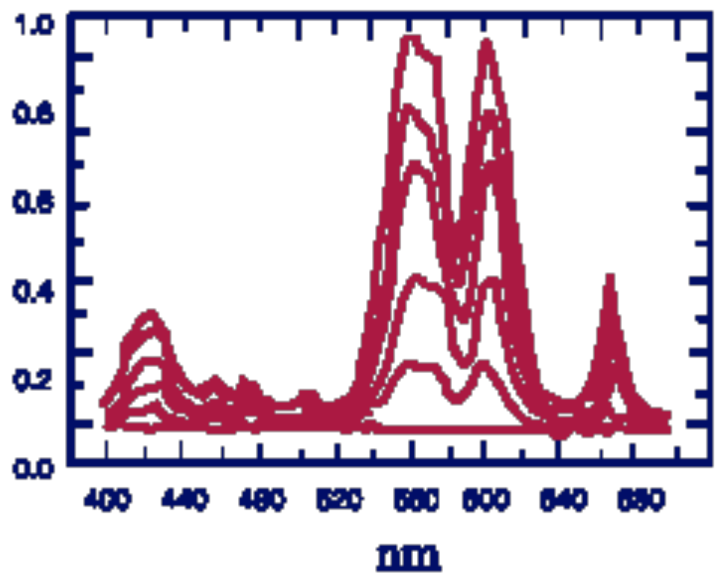
Ceric Titration for Plutonium Assay

- Interference by U, Np, Fe and potentially by other metallic elements that have multivalent ionic states
- Alkali metal and alkaline earth elements, Al, Cd, Hf, Zr, Sc, and Y do not interfere
- Typically performed using a 250 mg sample
- Method in use at LANL is automated
- Precision is 0.05% for the automated method

Ceric Titration

Concentration Measurements—Spectrophotometric Determination of Pu (III)

- Primarily used at LANL for analysis of $^{238}PuO_2$
- Absorbance of a 2 M HCl solution of Pu(III) is measured fro



Concentration Measurements—Spectrophotometric Determination of Pu (III) (cont.)

- Potential interferences from
  - Metallic elements that absorb from 510–640 nm (Np, Am, Fe, Th, Ga, Al tolerated at 1 wt% relative to Pu and Cr, Rh, Pd, Nd, Ru, and Au tolerated at 10 mg/g Pu),
  - Anions that hinder reduction of Pu(IV) to Pu(III)
- Method precision is 0.2%

Assay by Isotope Dilution Mass Spectrometry

- Uranium and Plutonium content can be determined using isotope dilution mass spectrometry (IDMS)
- Known amount of one isotope of an element (preferrably one that is not already present) added to unknown
  - Typically ^{233}U for uranium, ^{242}Pu or ^{244}Pu for plutonium
- Signal strength of each isotope measured relative to the isotope dilution tracer
  - $^{238}U/^{233}U$, $^{236}U/^{233}U$, $^{235}U/^{233}U$, $^{234}U/^{233}U$

Thermal Ionization Mass Spectrometer

Assay by Isotope Dilution Mass Spectrometry (cont.)

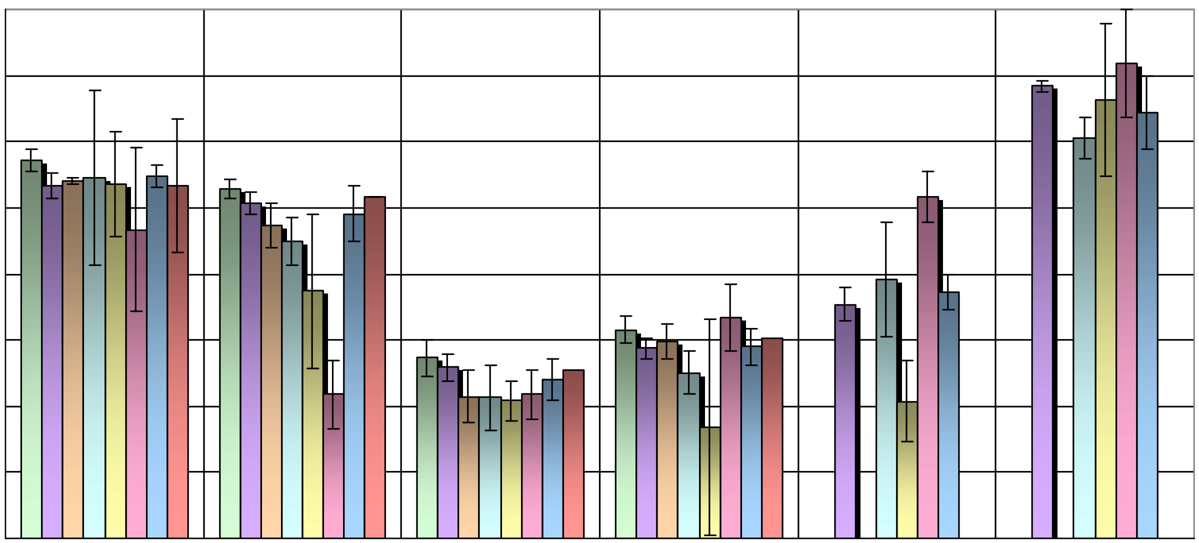
- Atoms of each analyte isotope determined from the known amount of tracer added and the measured isotope ratios
  - ^{238}U (atoms) = ^{233}U (atoms) x ^{238}U/^{233}U

- Convert atoms to grams
  - $$^{238}\text{U (g)} = \frac{^{238}\text{U (atoms)}}{6.02\text{e}23\ (\text{mol}^{-1})} \times 238\ (\text{g mol}^{-1})$$

- Sum isotopes to give total assay
  - Total U (g) = ^{238}U (g) + ^{236}U (g) ^{235}U (g) + ^{234}U (g)

Example Pu Assay Data and Comparison

- Pu Metal Exchange Program Data
  - Blind Round-robin QC program to evaluate Pu DA performance



Isotopic Analysis

- Thermal ionization mass spectrometry (TIMS) is benchmark method for determining U or Pu isotopic composition
  - Capable of high precision isotope ratio measurements
  - Abundance sensitivity dependent on instrument design, but 10^{-9} is possible
- Inductively coupled plasma mass spectrometry (ICP-MS) is also viable
  - Magnetic sector instrument preferable

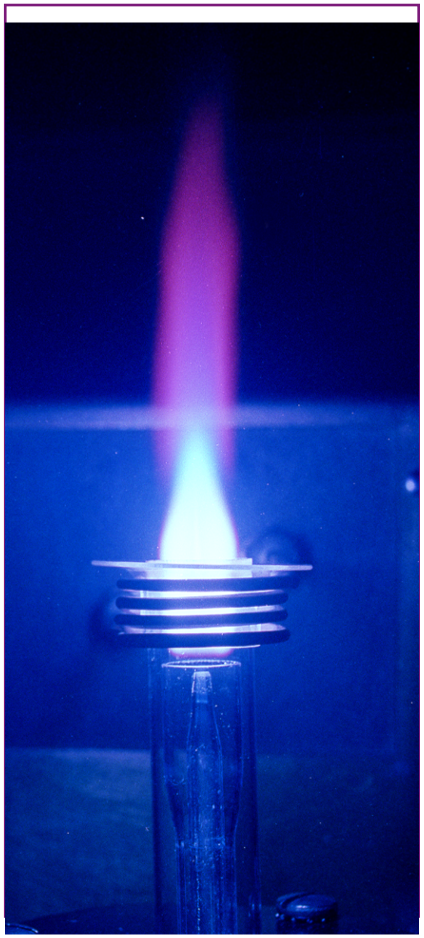
- 0.01 – 1 ng Pu for Pu isotopic analysis by TIMS
- 1 – 100 ng U for U isotopic analysis by TIMS

Pu Isotopics by Gamma-ray Spectrometry and TIMS

Radionuclide	Istotopic wt% by Gamma-ray Spectrometry	2 Sigma Uncertainty (Relative %)	Isotopic wt% by TIMS	2 Sigma Uncertainty (Relative %)
241Am	3.89E-04	5.03%	Not Determined	
238Pu	1.21E-04	22.54%	1.38E-04	3.35%
239Pu	9.37E-01	3.01%	9.39E-01	0.25%
240Pu	6.09E-02	7.85%	5.92E-02	0.57%
241Pu	1.33E-03	3.04%	1.33E-03	0.94%
242Pu	Not Determined		3.65E-04	1.43%

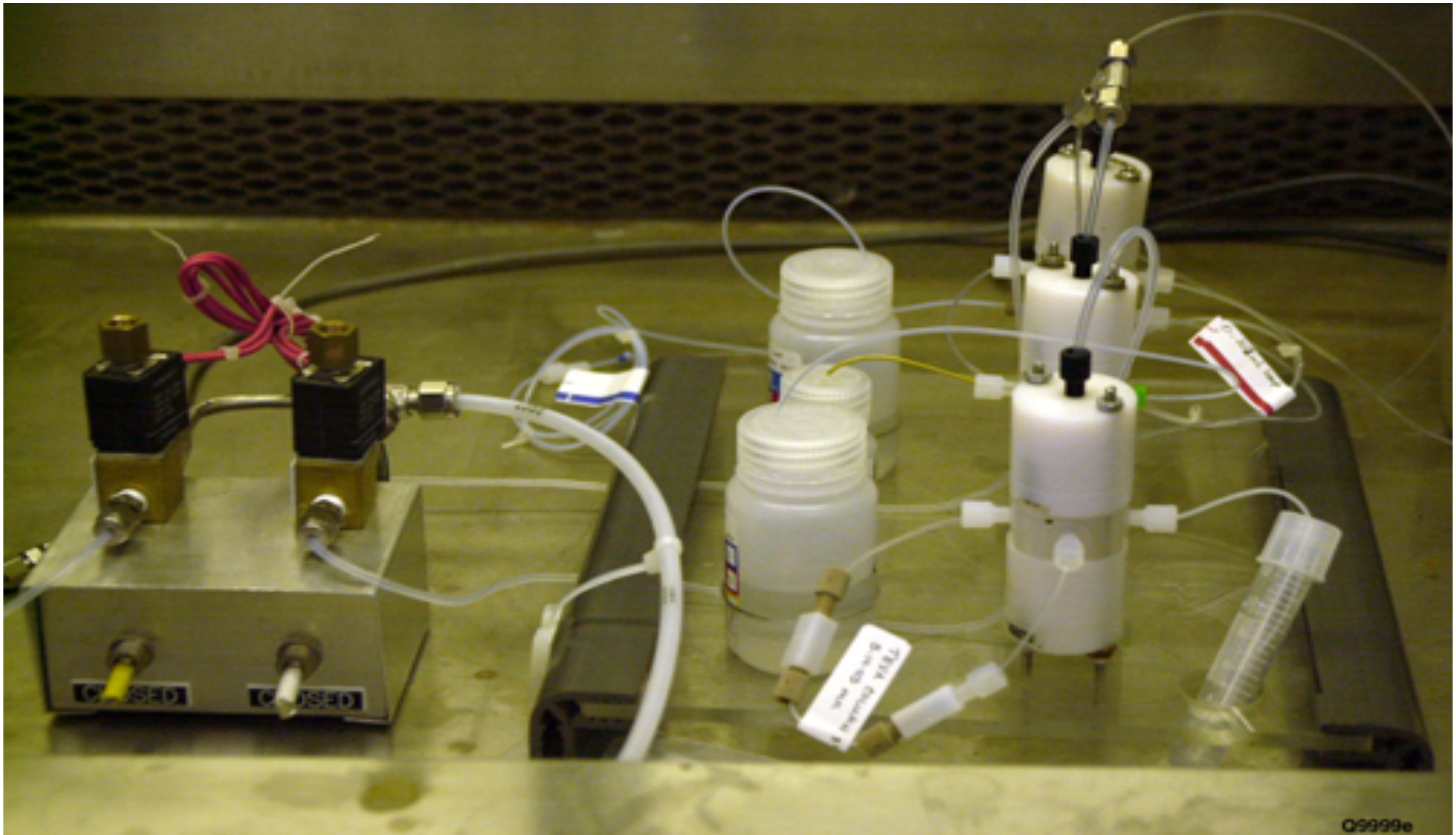
Trace metal impurity analysis

- Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)
  - Primarily used for impurities analysis
  - Provides less precise (~10%) measurement of U, Pu or elemental concentrations
  - Requires sample dissolution
  - Subject to spectral interferences (chemical separation may be required)
  - Can analyze many elements at one time
  - Automated instrumentation



Instruments in Hoods & Gloveboxes

Gas Pressurized Extraction Chromatography Set-Up----- Footprint 12 x 18 inches



Plutonium Oxalate Precipitate (POP) Separation (*Courtesy AWE*)

Samples can be either plutonium metal/alloy dissolved in HCl or aliquots of prepared plutonium chloride bulk solution.

Plutonium chloride sample solution is reduced using hydroxylamine hydrochloride.

Pu 4+ present is converted to the 3+ oxidation state

Three oxalate ions combine with two Pu III ions to form plutonium oxalate precipitate. Am is also precipitated.

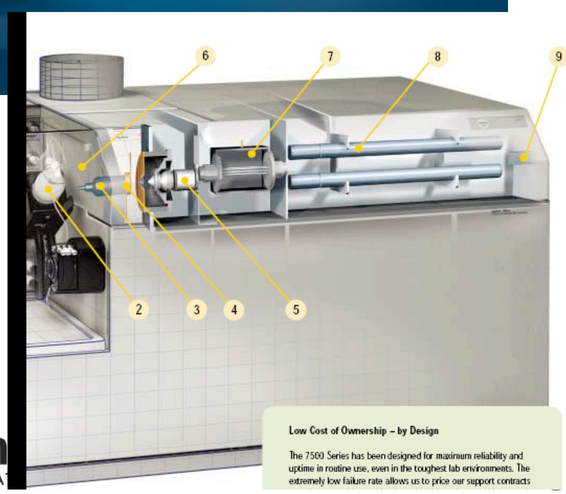
$Pu_2(C_2O_4)_3 .10H_20$

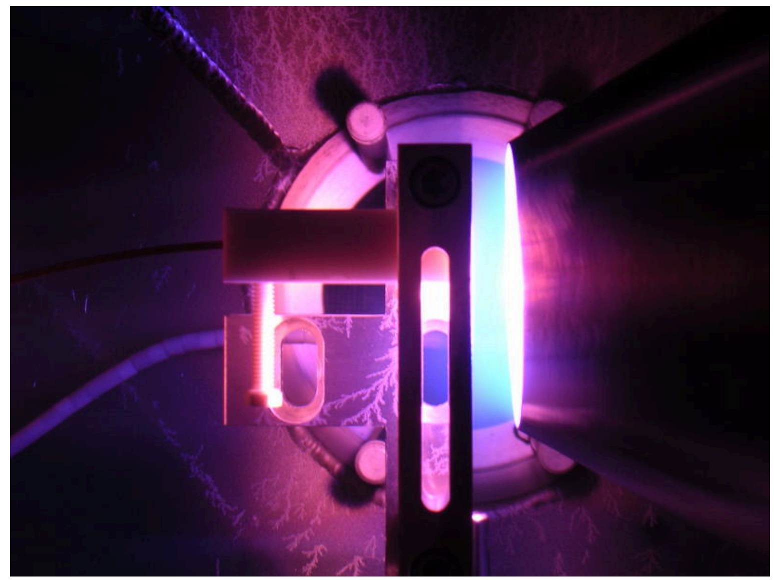
The precipitate settles out.

Centrifugal separation compacts the precipitate allowing easy recovery of the trace elements.

Analytical Tool – Mass Spectrometry

Inductively Coupled Plasma



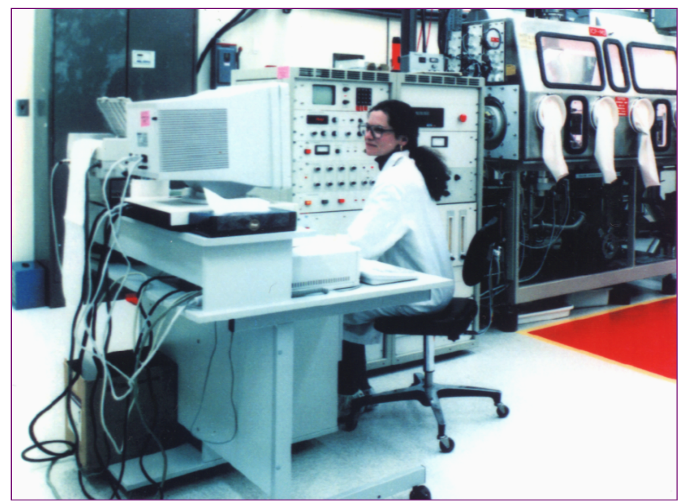


plasma: ionized gas, brilliant color depends on the type of gas

Trace Impurities by ICP-MS

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

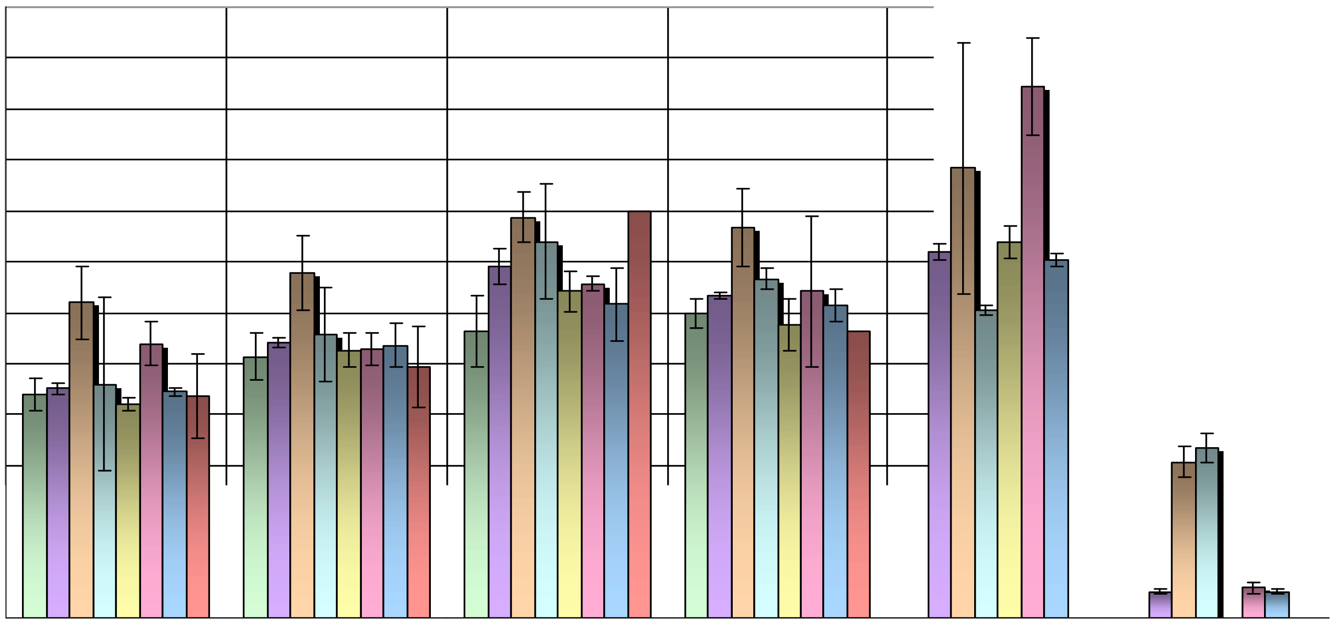
- Sample must be dissolved before introduction into the instrument
  - Complementary interferences
  - Determination of 70+ elements
  - Precisions typically 5 – 20%



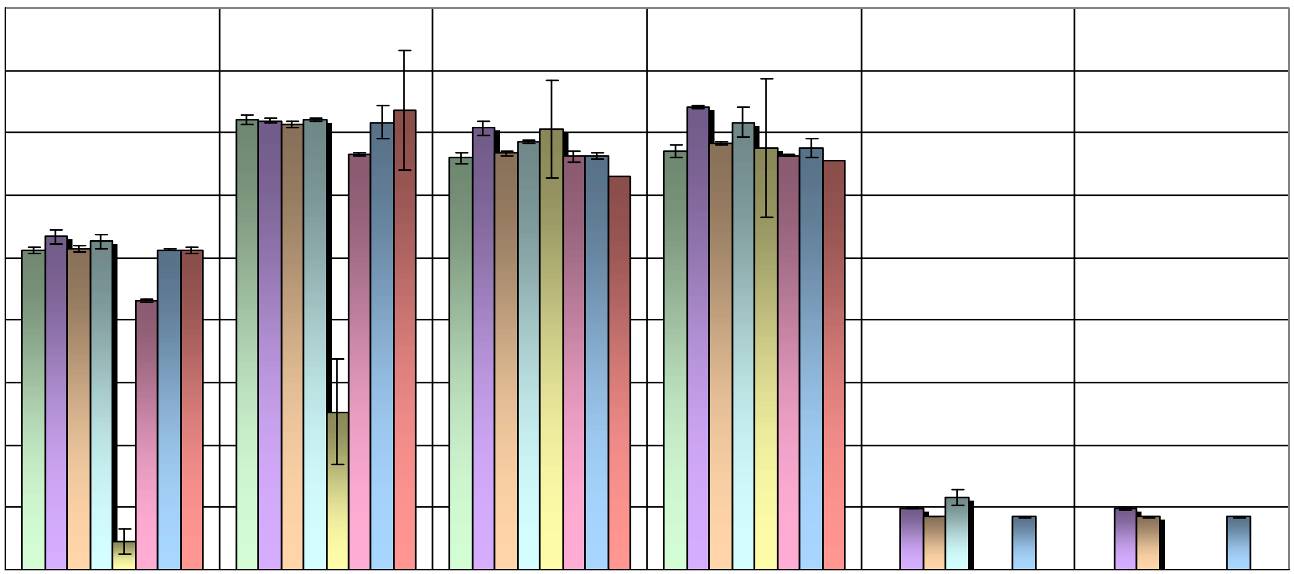
Analytical Tools for Trace Analysis

Element	Method	Sample (ppm)
Al	ICP-AES	506
Ca	ICP-AES	2590
O	IC	15.7%
Fe	ICP-AES	2530
Mg	ICP-AES	1670
Na	ICP-AES	8120
Si	ICP-AES	116
Sr	ICP-MS	144
P	ICP-AES	1570
Pu	TIMS	24.7
Np	ICP-AES	0.5
Zn	ICP-AES	44

Example Data: Iron in Plutonium



Example Data: Uranium in Plutonium



Example Safeguards Application

- The time elapsed since a material was last radiochemically purified can be measured using radiochronometry

- Important measurement to verify facility operating history
- Three chronometers measured by TIMS

Age Determination using Radiochronometers

Sample: PuO_2

Plutonium oxide for MOX Fuel Production

Nuclide	wt %	Nuclide	wt %
^{238}Pu	0.0077	^{234}U	1.475
^{239}Pu	93.7677	^{235}U	73
^{240}Pu	6.1317	^{236}U	17.1
^{241}Pu	0.0737	^{238}U	8.285
^{242}Pu	0.0191		

Ratio	Measured Age* (years)
$^{238}Pu/^{234}U$	0.514
$^{239}Pu/^{235}U$	0.542
$^{240}Pu/^{236}U$	0.528

Average Age: 0.528 years

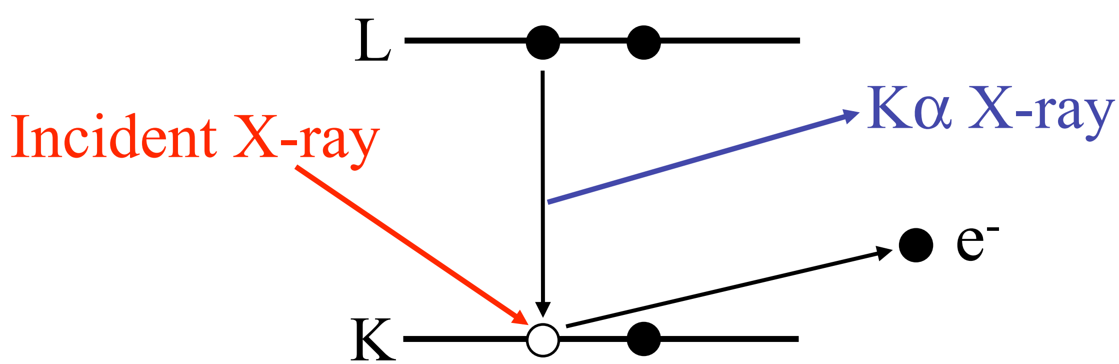
Typical concentration of ^{241}Pu is 0.14%.
In this sample, ^{241}Pu is 0.0737%.

Half-life of ^{241}Pu is 15 years.

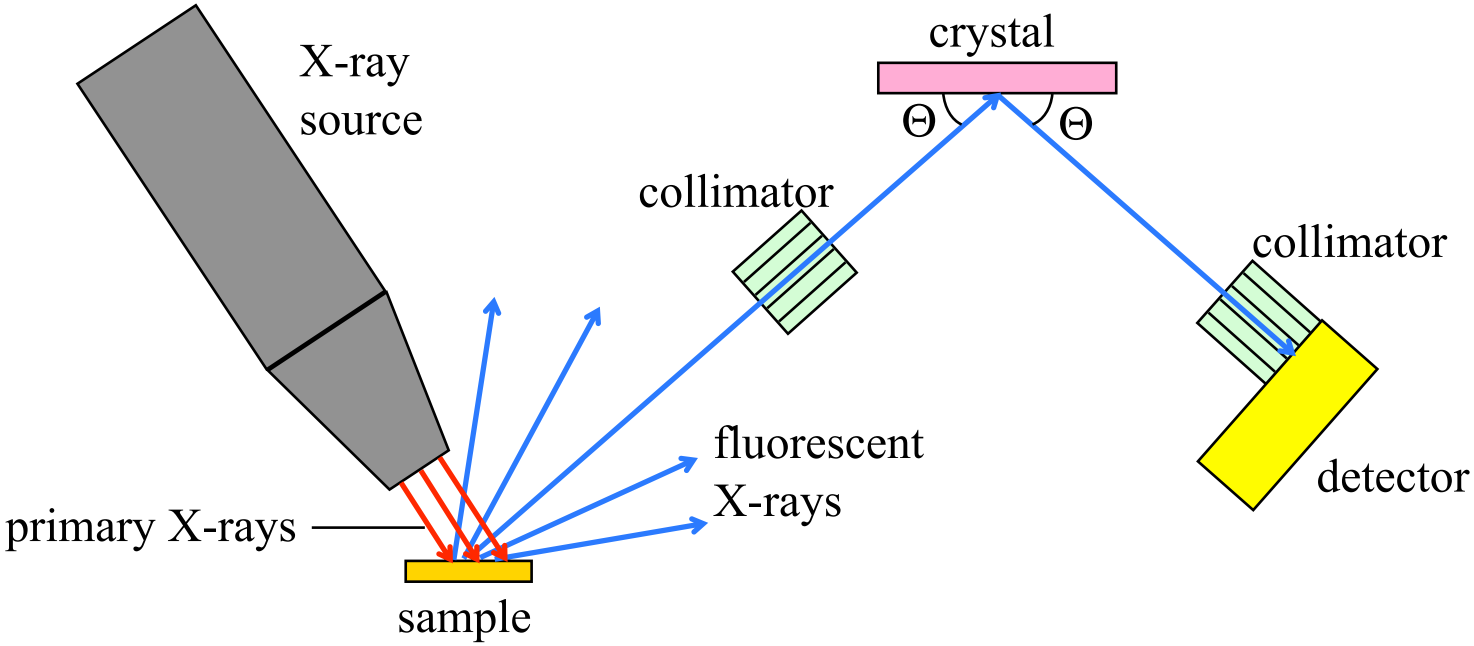
DA for IAEA for Environmental Safeguards

- Environmental safeguards sampling and analysis is a powerful method for verifying declared operations at safeguards facilities
- Analyses completed at IAEA Network of World Analytical Laboratories (NWAL)
- Swipe Analysis
  - NDA Gamma-ray Spectrometry
  - X-ray fluorescence
  - Uranium Assay by ICP-MS or ID TIMS, Isotopics by TIMS
  - Plutonium Assay and Isotopics by ID TIMS
- Rigorous QA program
  - Process blank(s) run with every batch
  - Blind QC samples analyzed at least once per year
- Much smaller quantities of material than traditional accountability measurements
  - Uranium: 1 ng – 10 mg
  - Plutonium: 1 fg – 10 ng

X-ray Fluorescence (XRF)



WDXRF INSTRUMENT

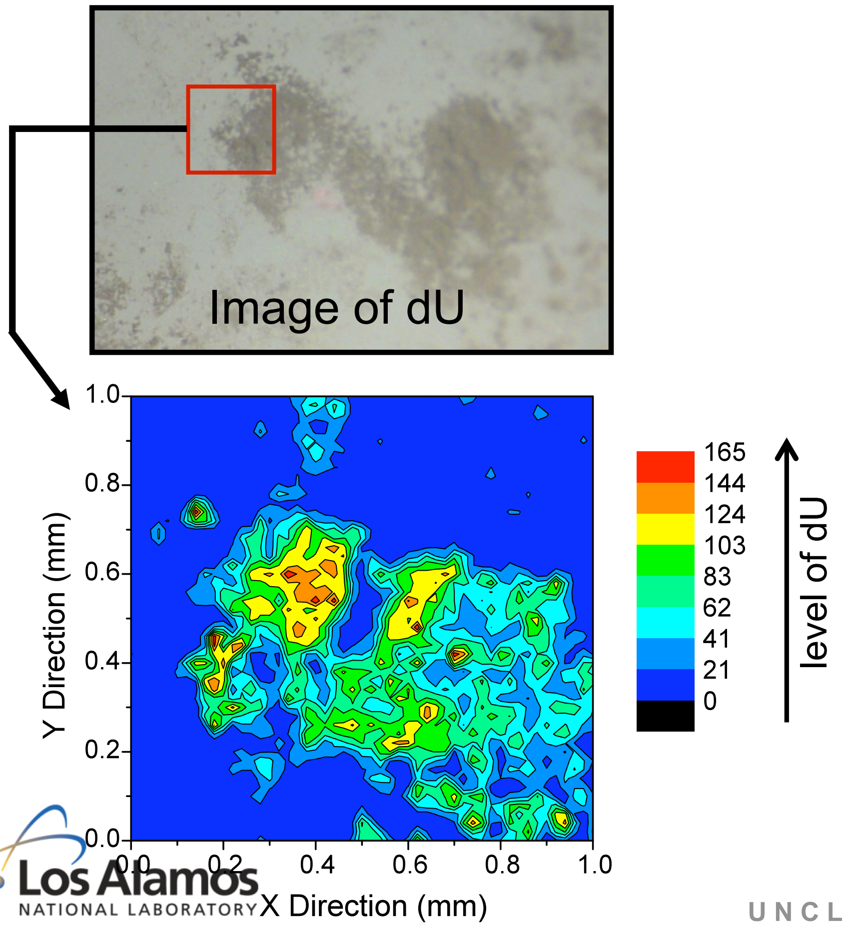


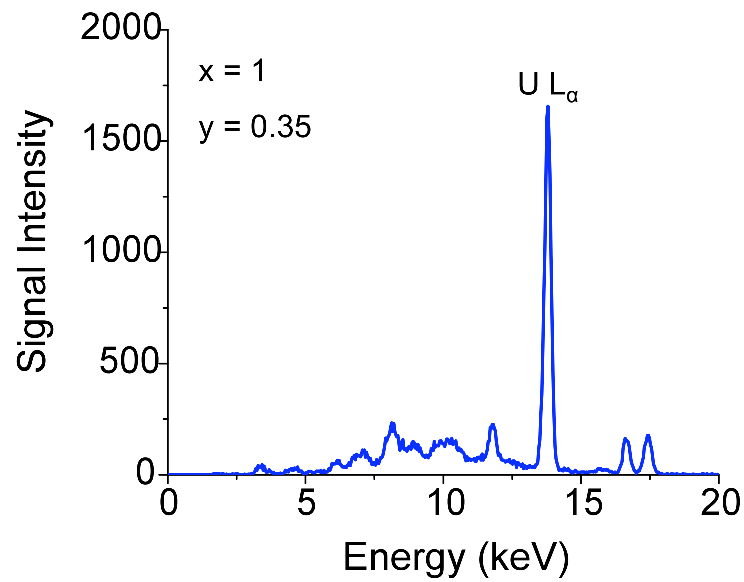
- PANalytical PW2404 XRF Spectrometer
- Wavelength-dispersive
- 4000 W rhodium X-ray anode
- Rad samples sealed inside cells for analysis

Bulk Characterization

Elemental Composition and 2d Mapping

Analysis of dU by Confocal MXRF





Spectrum collected at point x = 1 and y = 0.35. These coordinates correlated to the contour plot (100 s int.).

Conditions: 50 kV, 0.5 mA, (P = 25 W)

RC-45 Clean Chemistry Facility

- 10,000 sq. ft. of clean laboratory space (Class 10,000 – Class 10)
- Ultra-low level analysis of actinides in environmental and biological samples
- State-of-the-art mass spectrometry instrumentation
- Expertise in the development and implementation of new analytical procedures

High-resolution Multi-collector Inductively Coupled Plasma Mass Spectrometer

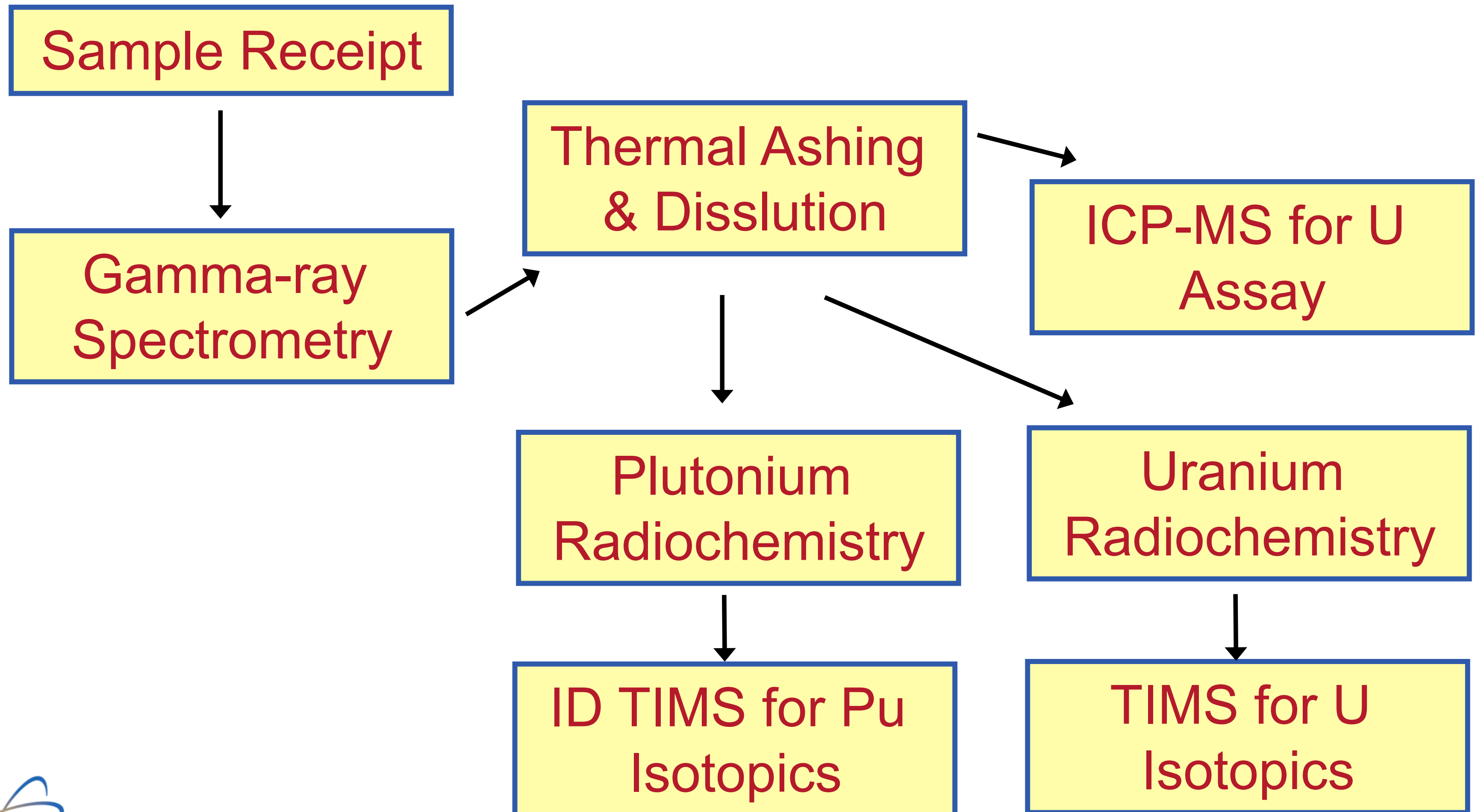
Core Capabilities

Clean Room Radiochemistry Laboratory

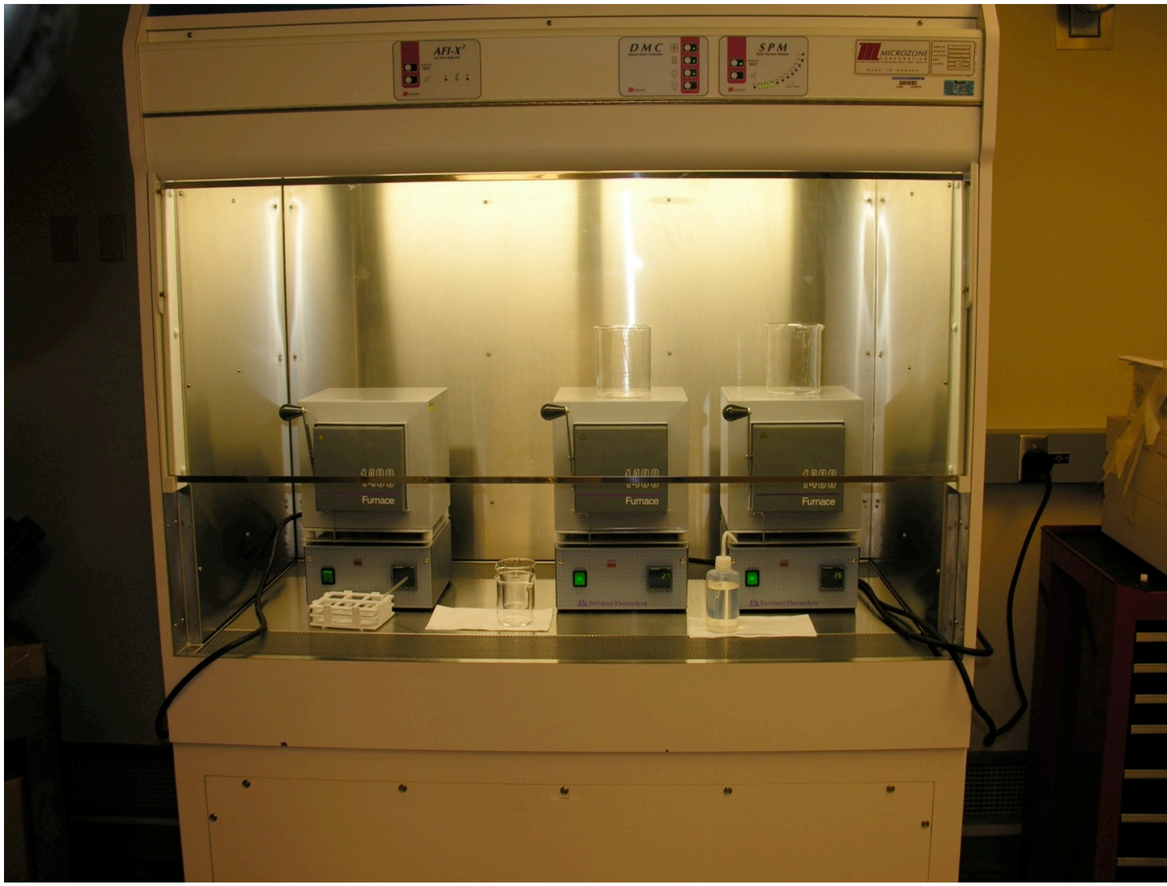
- Ultra-sensitive actinide isotopic analysis (< 10^6 atoms) using thermal ionization mass spectrometry (TIMS)
- Radiochemical separations using ion-exchange and ion-extraction chromatography and capillary electrophoresis
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for rapid isotopic measurements for actinide analysis as well as age dating using U-series, Pu, Am, and Np measurements.

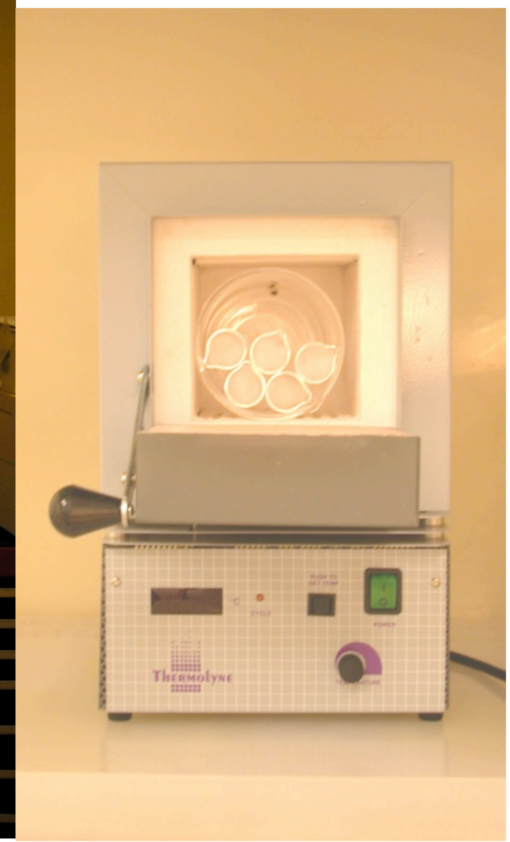
- Protection of facility from contamination is paramount!

NWAL Swipe Analysis Flow Sheet



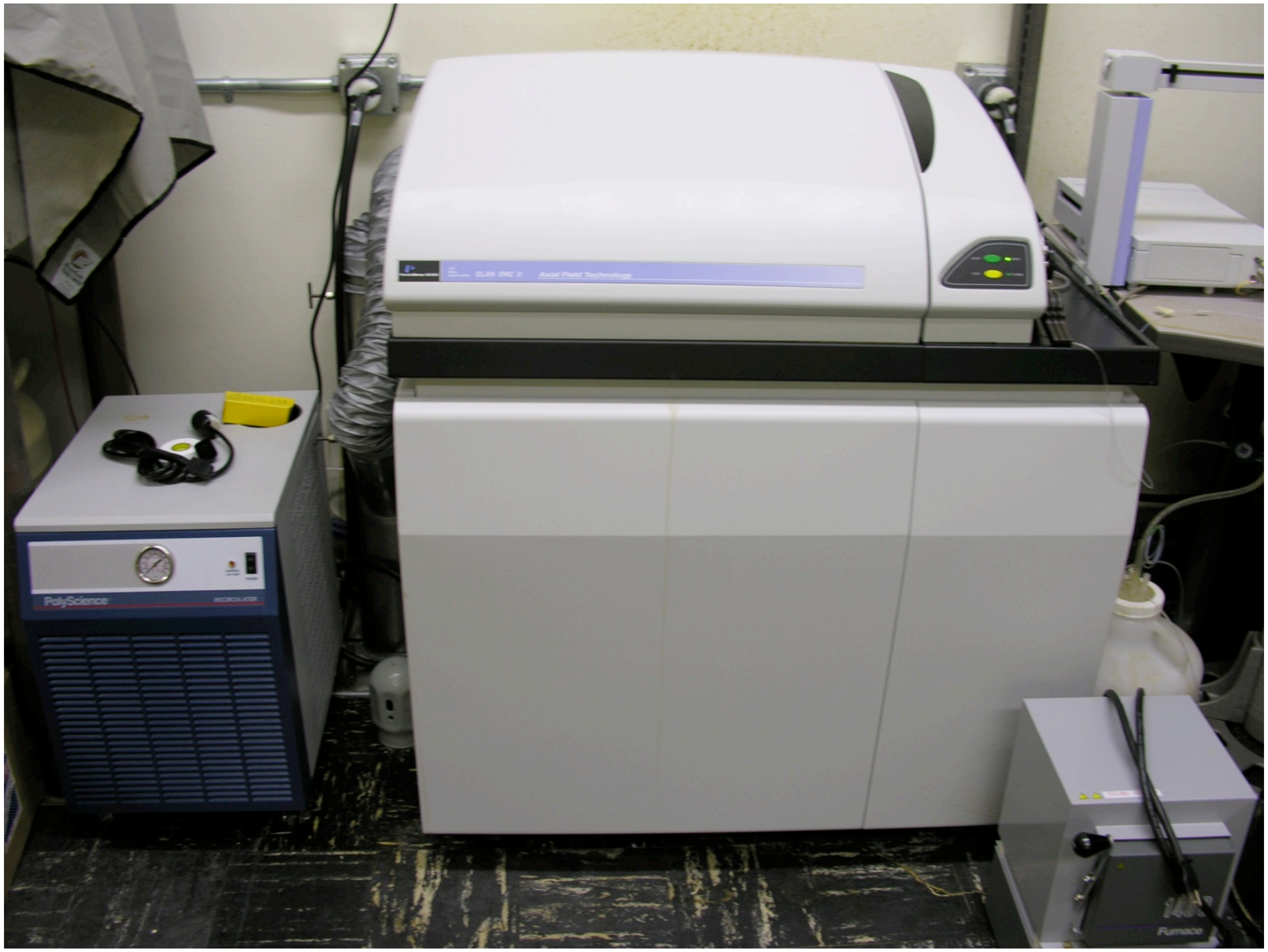
Cleanroom Ashing Setup





Alpha Survey

ICP/MS for Uranium Assay

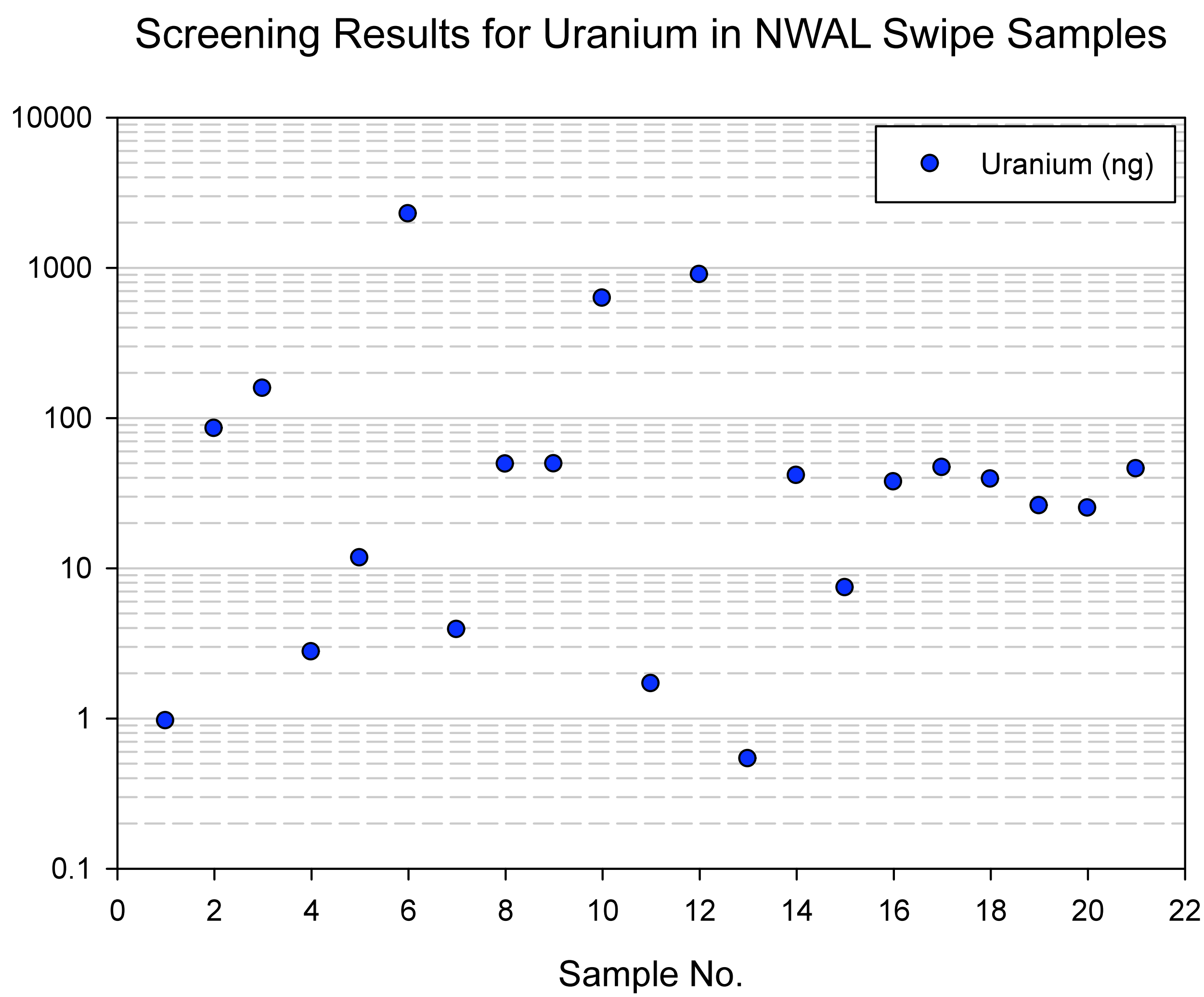


ICP-MS Screening Protocol

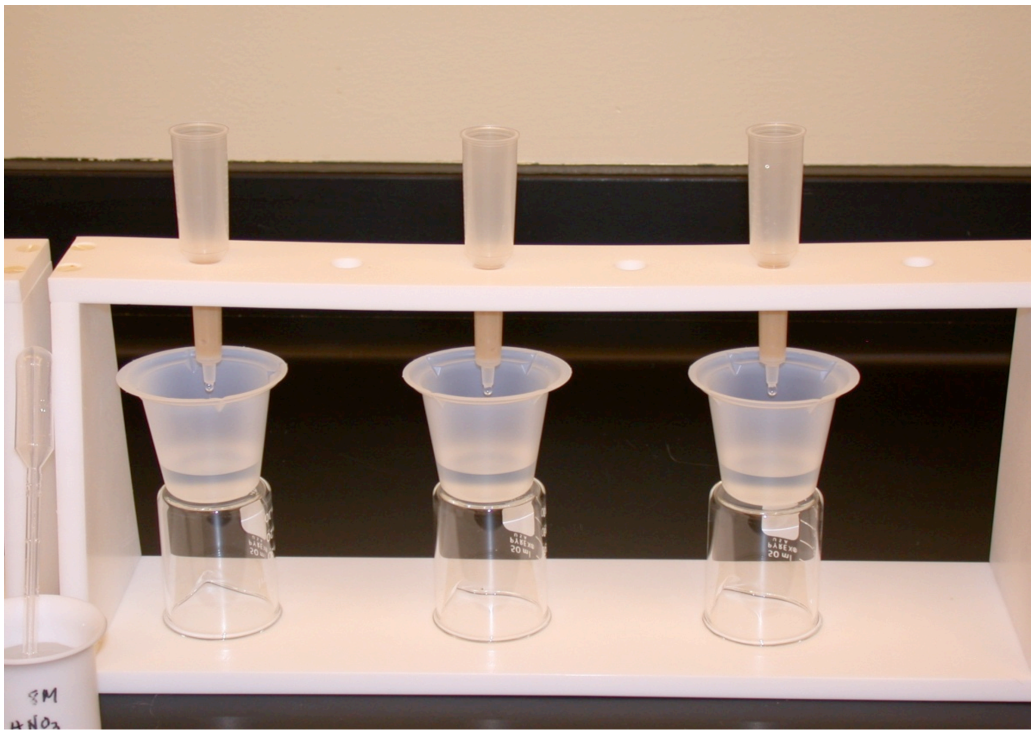
- GOAL: Estimate total U, $^{235}U/^{238}U$, Pu present
- External calibration
- Correction for instrumental drift:
  - Internal standardization ^{115}In
  - External drift monitoring:
    - Identical concentration standards measured at beginning, middle and end of a run.
- Screen for the following radionuclides:

^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu

Screening Results for Total Uranium



Pu Radiochemistry



Pu Radiochemistry

Spike Aliquot with ^{242}Pu or ^{244}Pu, convert to 8M HNO_3

↓

1 mL AG1x8 50-100 Cl^- Anion Column

↓

0.5 mL AG1x8 50-100 Cl^- Anion Column

↓

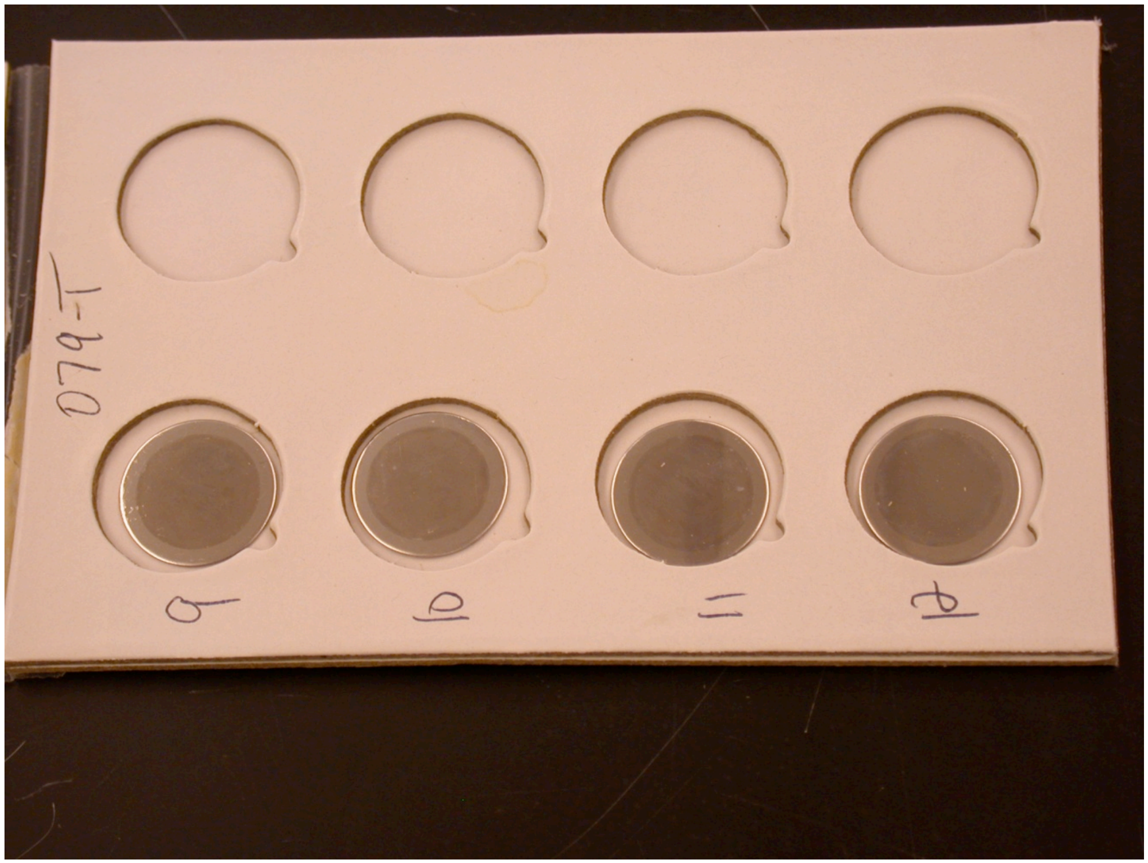
Add $NaHSO_4$ and Wet ash with HNO_3

↓

Electrodeposit Pu onto planchet

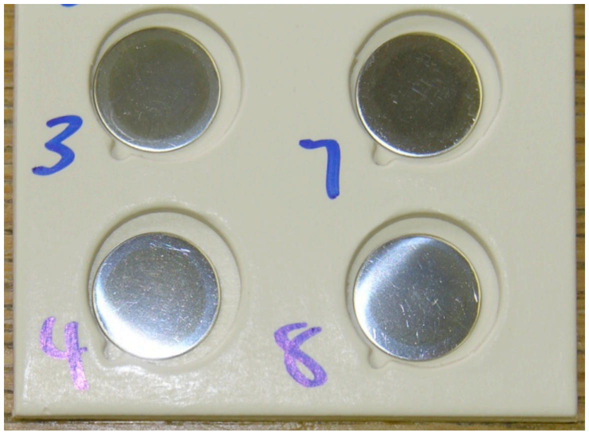
Pu Sample Electrodeposition

Electrodeposited Samples

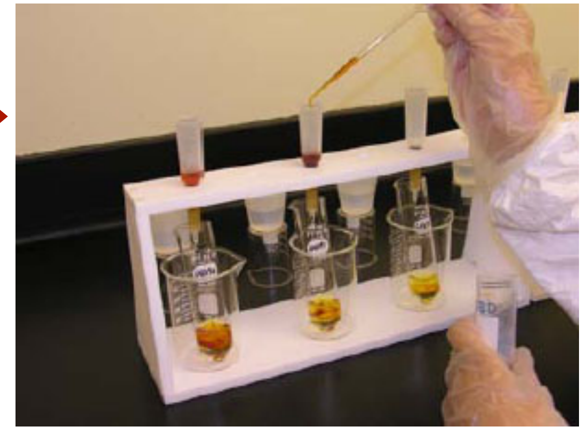


Alpha Spectroscopy Analysis

TIMS Prep Radiochemistry



Dissolve Pu off Planchets



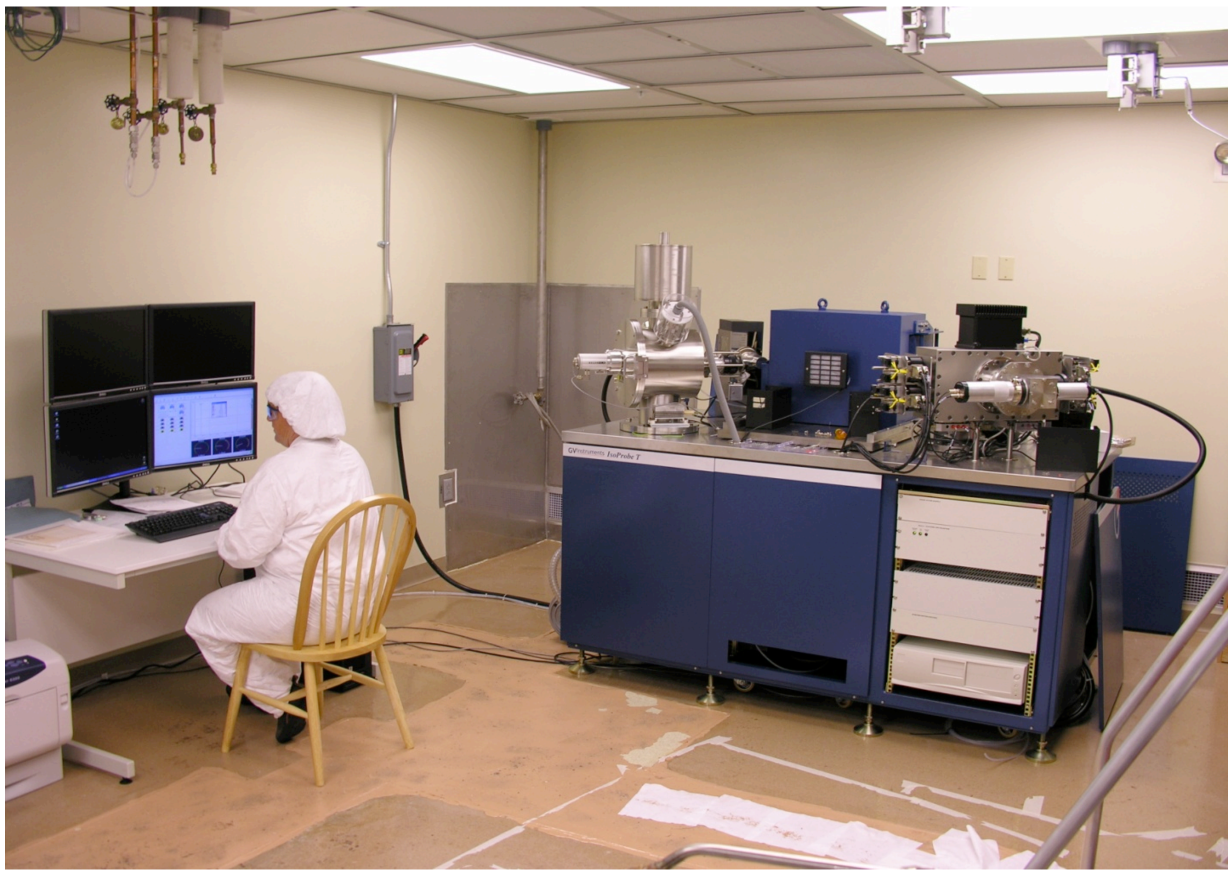
Radiochemical Separations

Wet Ash Pu

Electrodeposit Pu for TIMS

Multi-Collector TIMS

- New IsotopX Multi-Collector TIMS for NWAL program



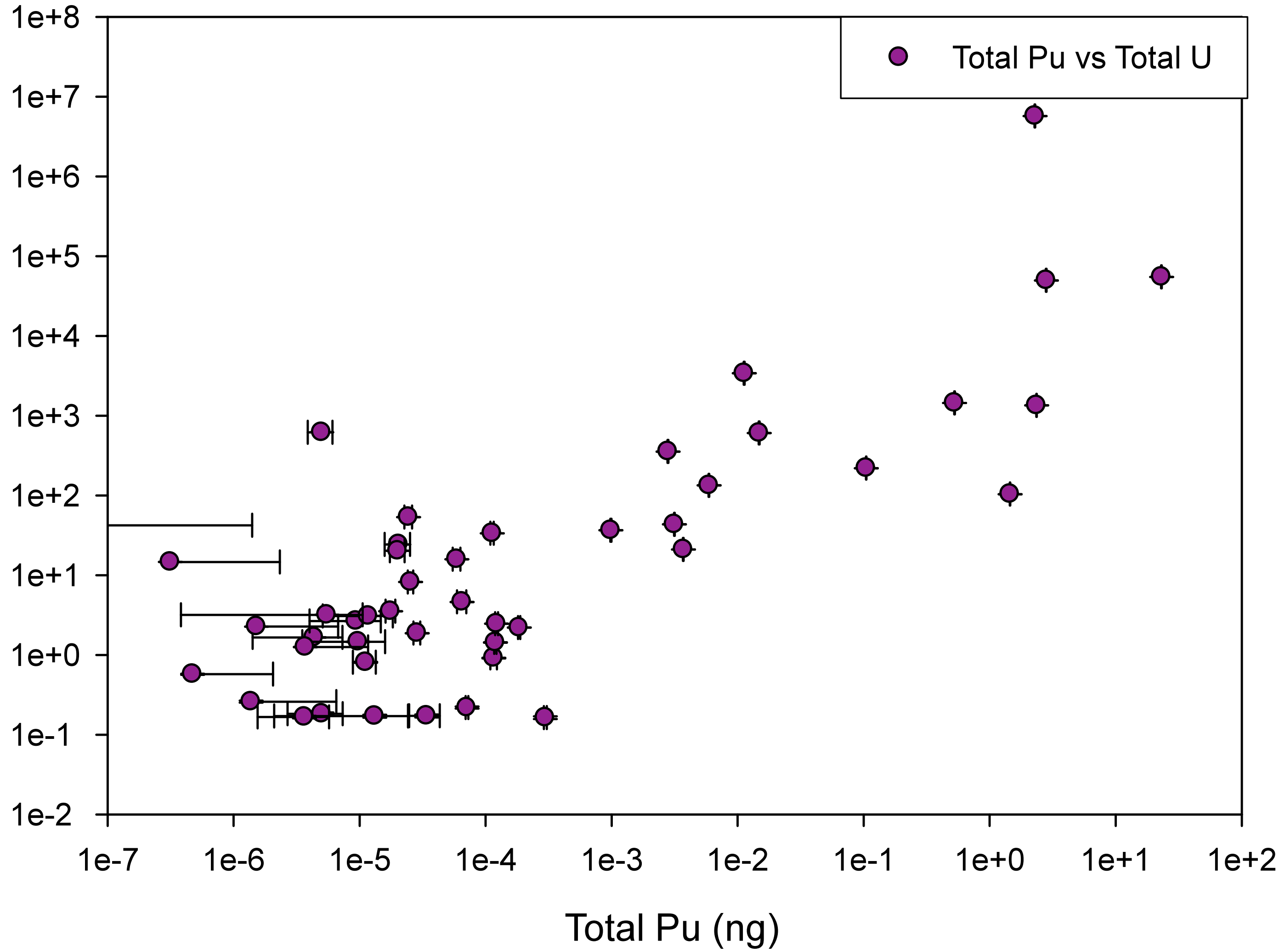
Challenges with Environmental Safeguards DA

- Uranium: 1 ng – 10 mg
  - Huge dynamic range – 7 orders of magnitude!
  - Low end of range is limited by background U in swipes

- Uranium enrichment also challenging
  - Everything from DU up to HEU in samples

- Plutonium: 1 fg – 10 ng
  - Also has a huge dynamic range covering 7 orders of magnitude
  - Low end of range is limited by instrumental detection limits

Total U and Pu in NWAL Samples

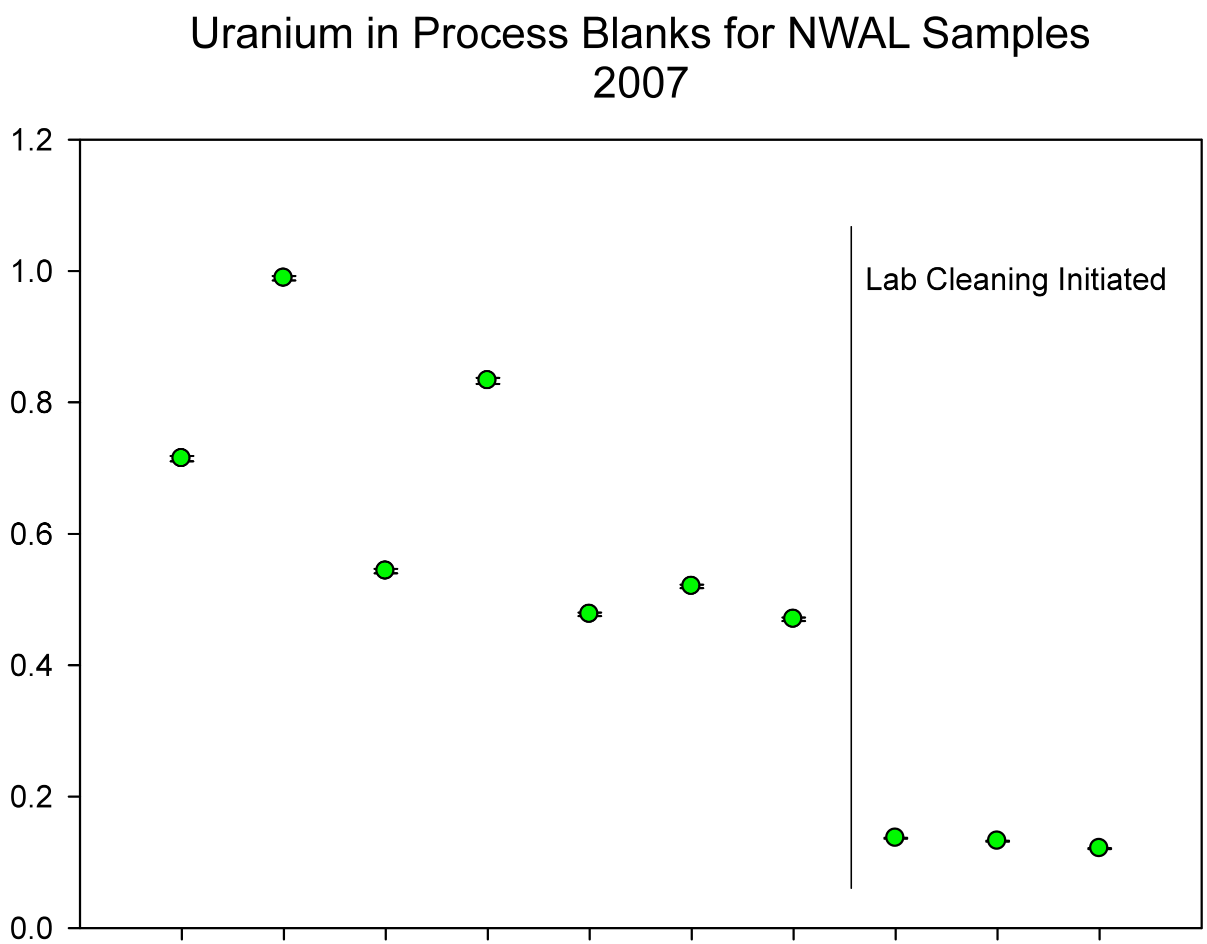


Samples with High Levels of Uranium

- High U in samples will affect the process blank

Sample	Total U (ng)	$^{235}U/^{238}U$	Cross-Contamination Factor for Process Blank
Sample 1	49,600	8.55	1 ppm
Sample 2	533,400	0.00481	15 ppm

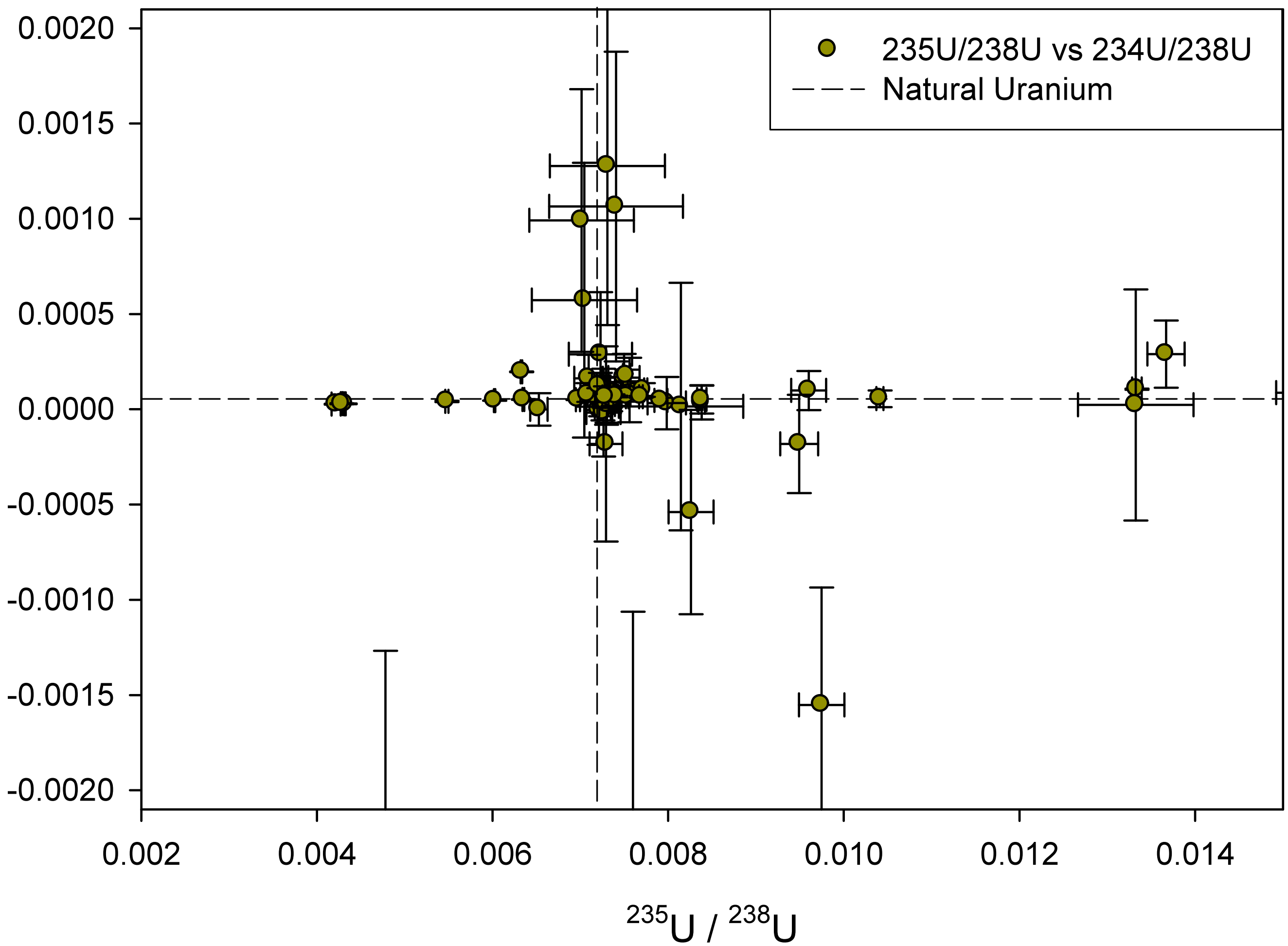
Blank Problems from High U Samples



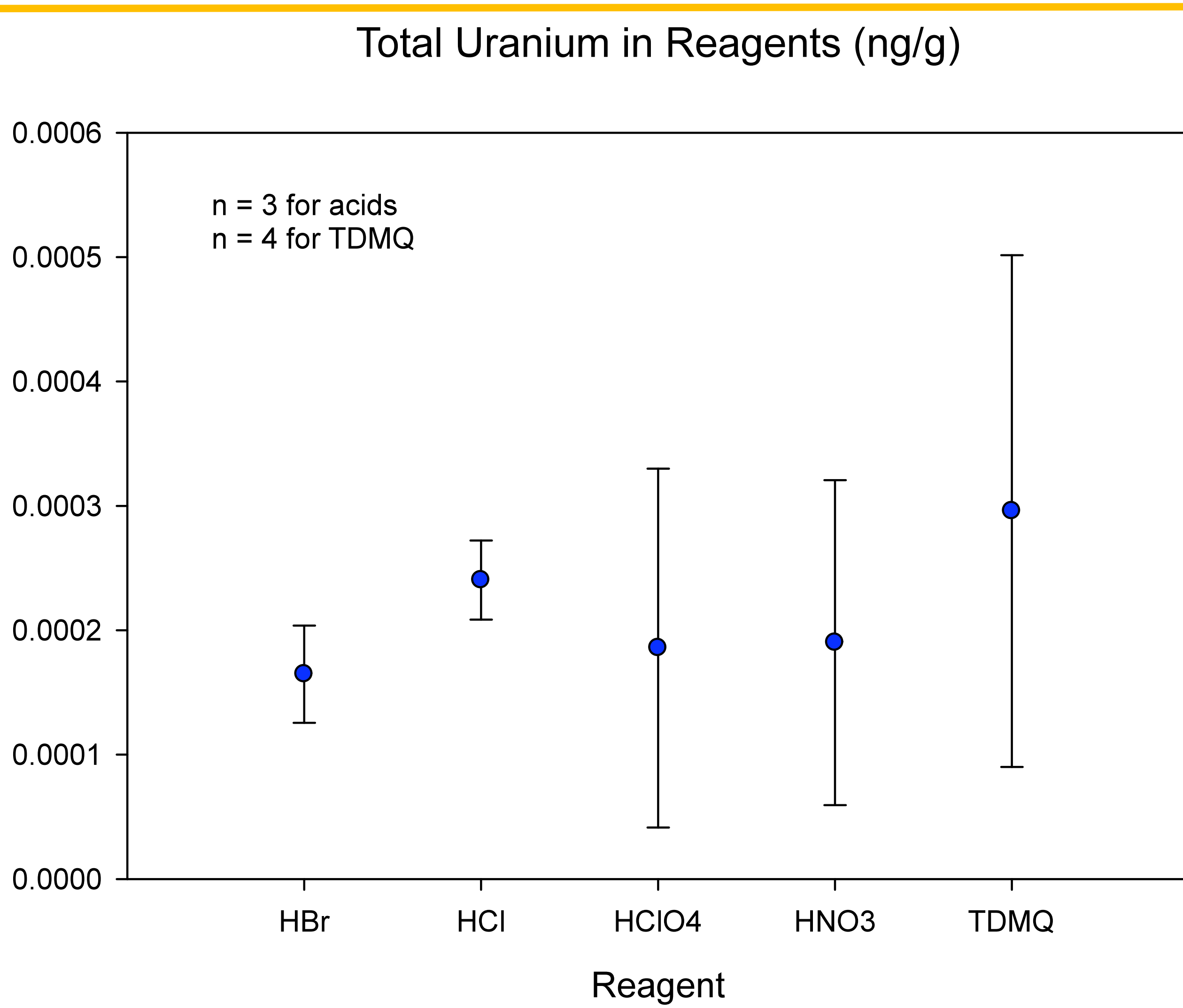
Uranium Blanks – Pushing the Limits

- Thorough understanding of uranium blank contribution needed for precise $^{234}U/^{238}U$ and $^{235}U/^{238}U$ measurement
  - Many samples near natural, low U content
- Careful evaluation of U blank sources
  - Reagents
  - Anion exchange resin
  - Furnace type
  - Radiochemistry laboratory

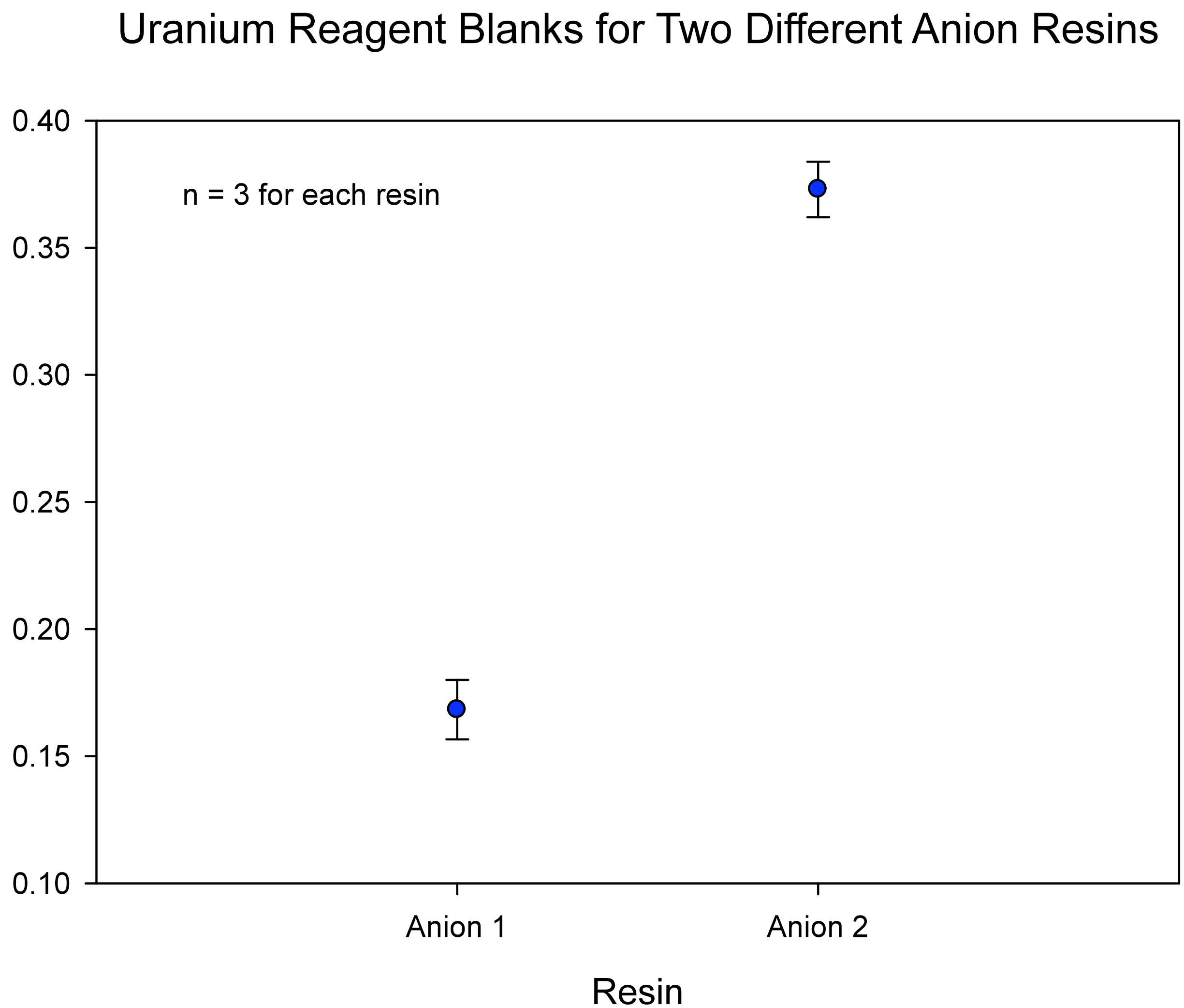
U Isotope Ratios Near Natural



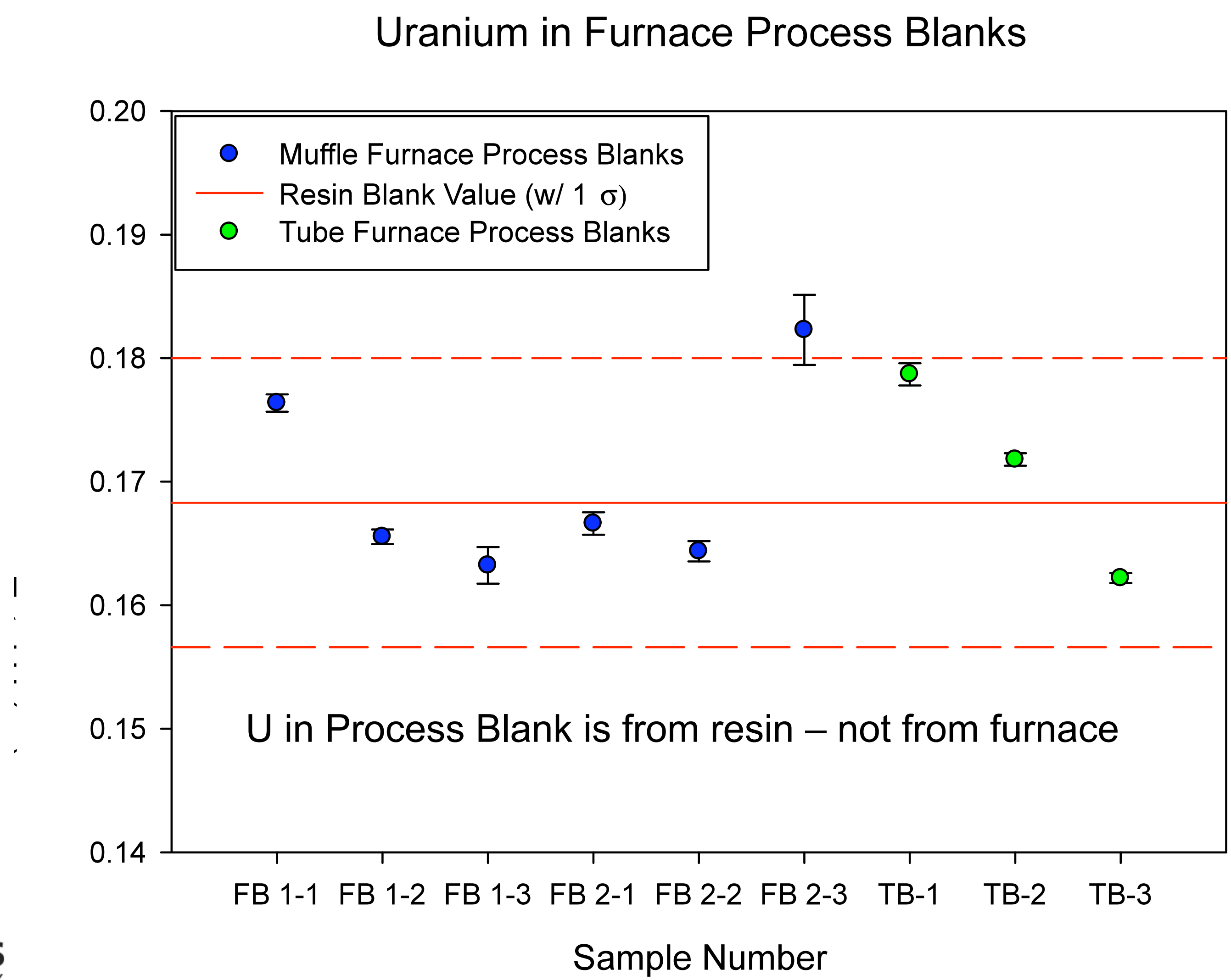
Uranium in Reagents



Uranium in Anion Exchange Resin



Uranium in Process Blanks



Blind QC Program

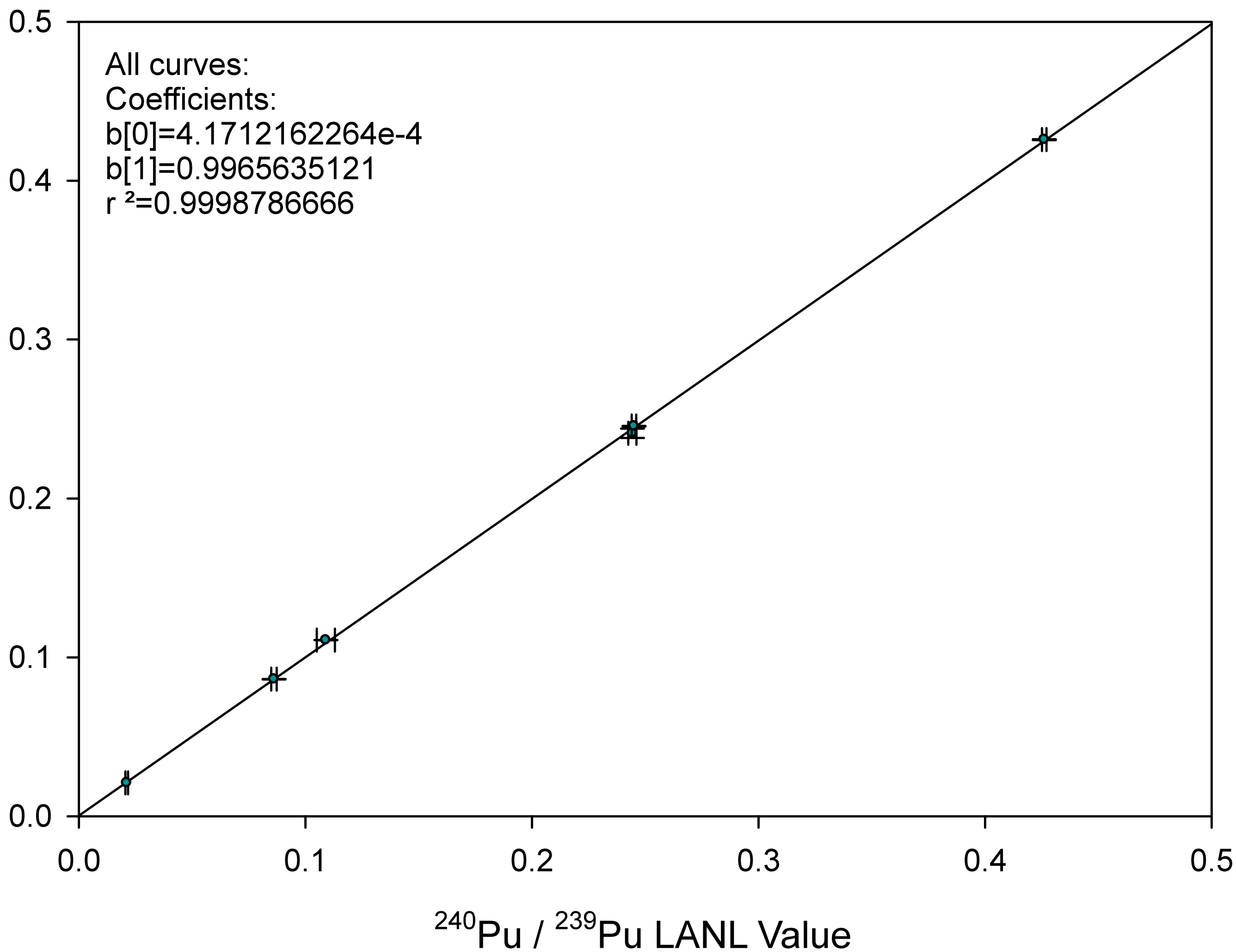
- 3 Blind QC swipes distributed each year
  - Prepared by LLNL

- Only certified for isotopic compositions
  - ^{234}U / ^{238}U, ^{235}U / ^{238}U, ^{236}U, ^{238}U
  - ^{240}Pu / ^{239}Pu, ^{241}Pu / ^{239}Pu, ^{242}Pu / ^{239}Pu

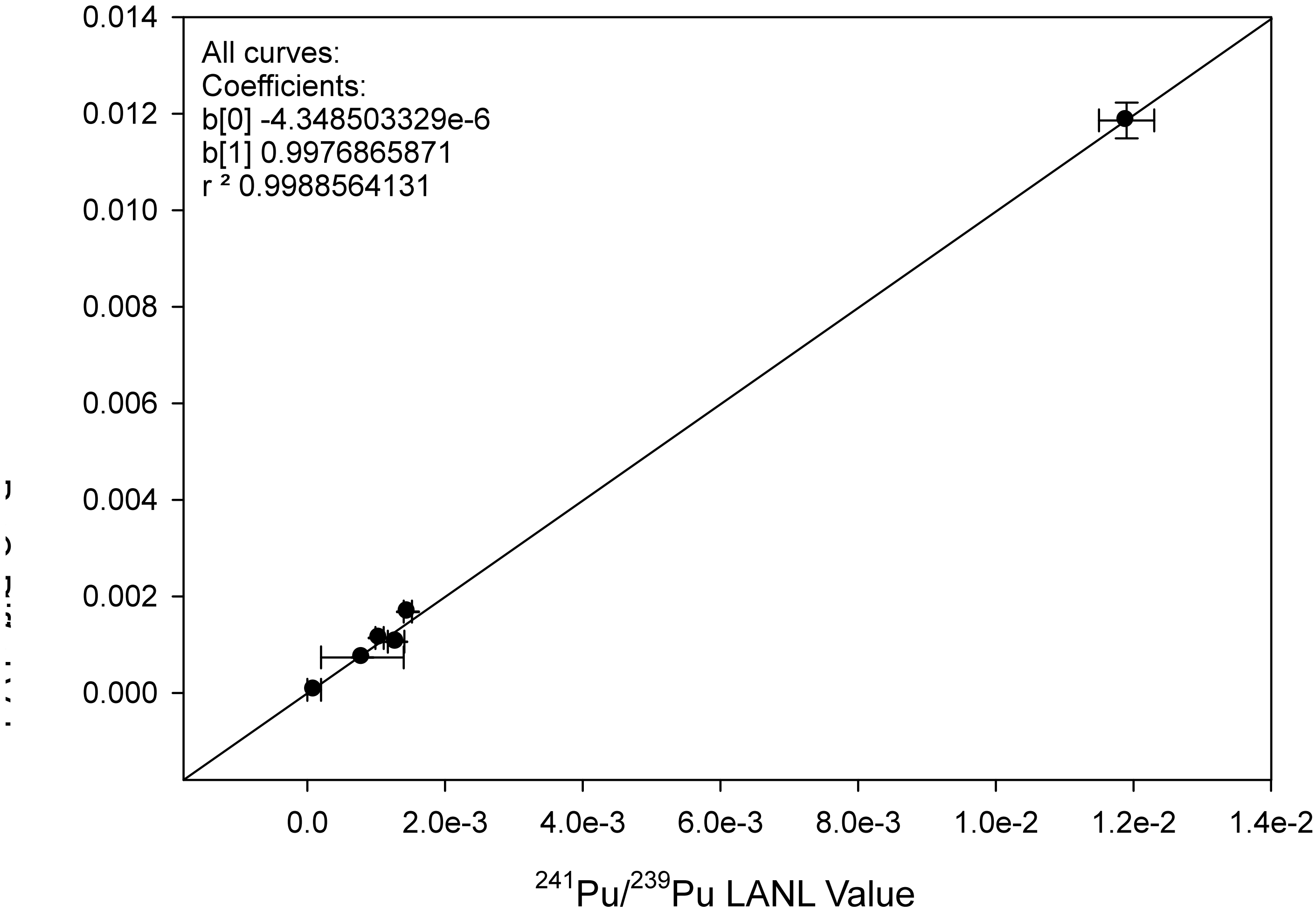
- Total U and Pu only approximate

- No fission products

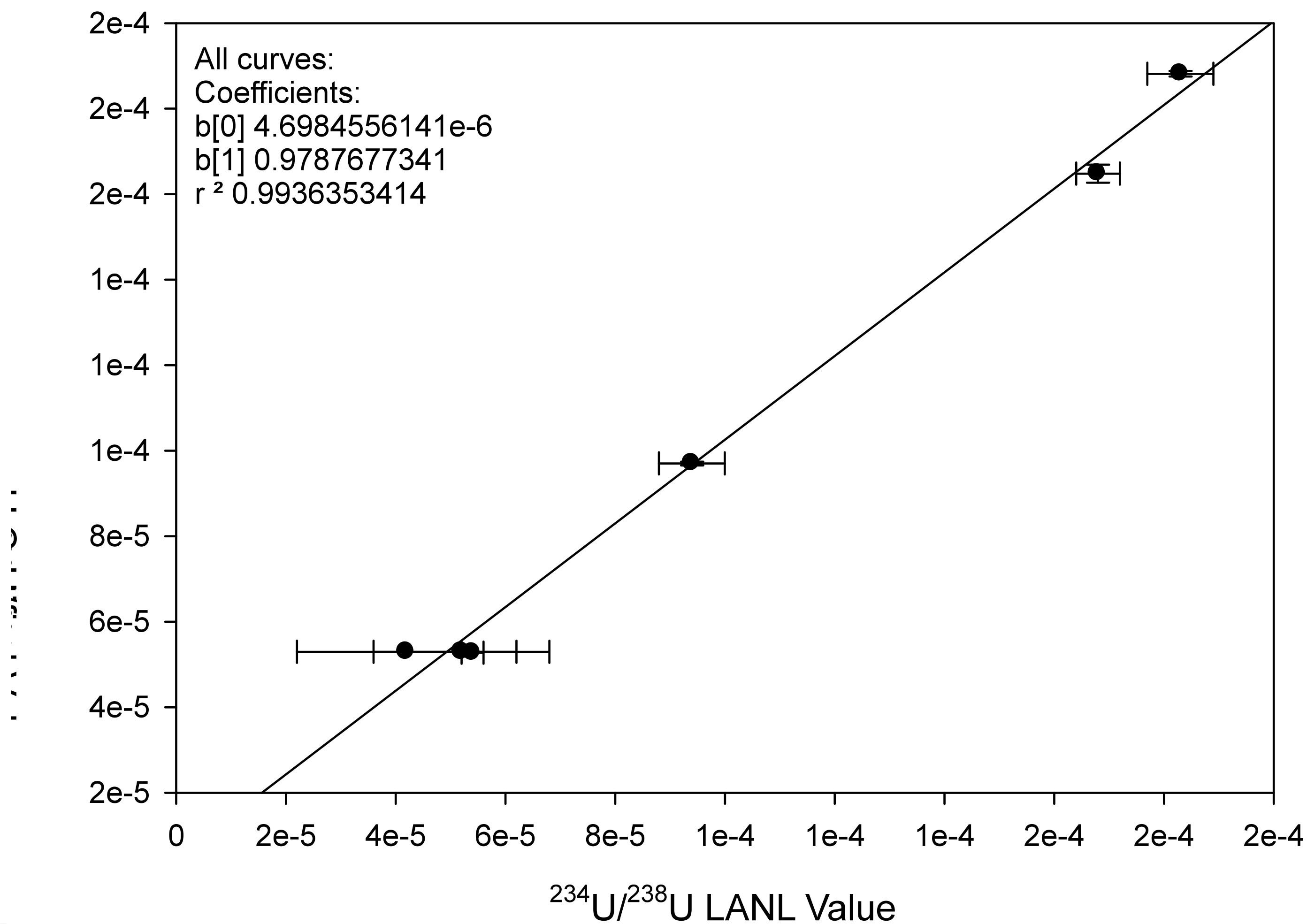
^{240}Pu / ^{239}Pu Blind QC Performance



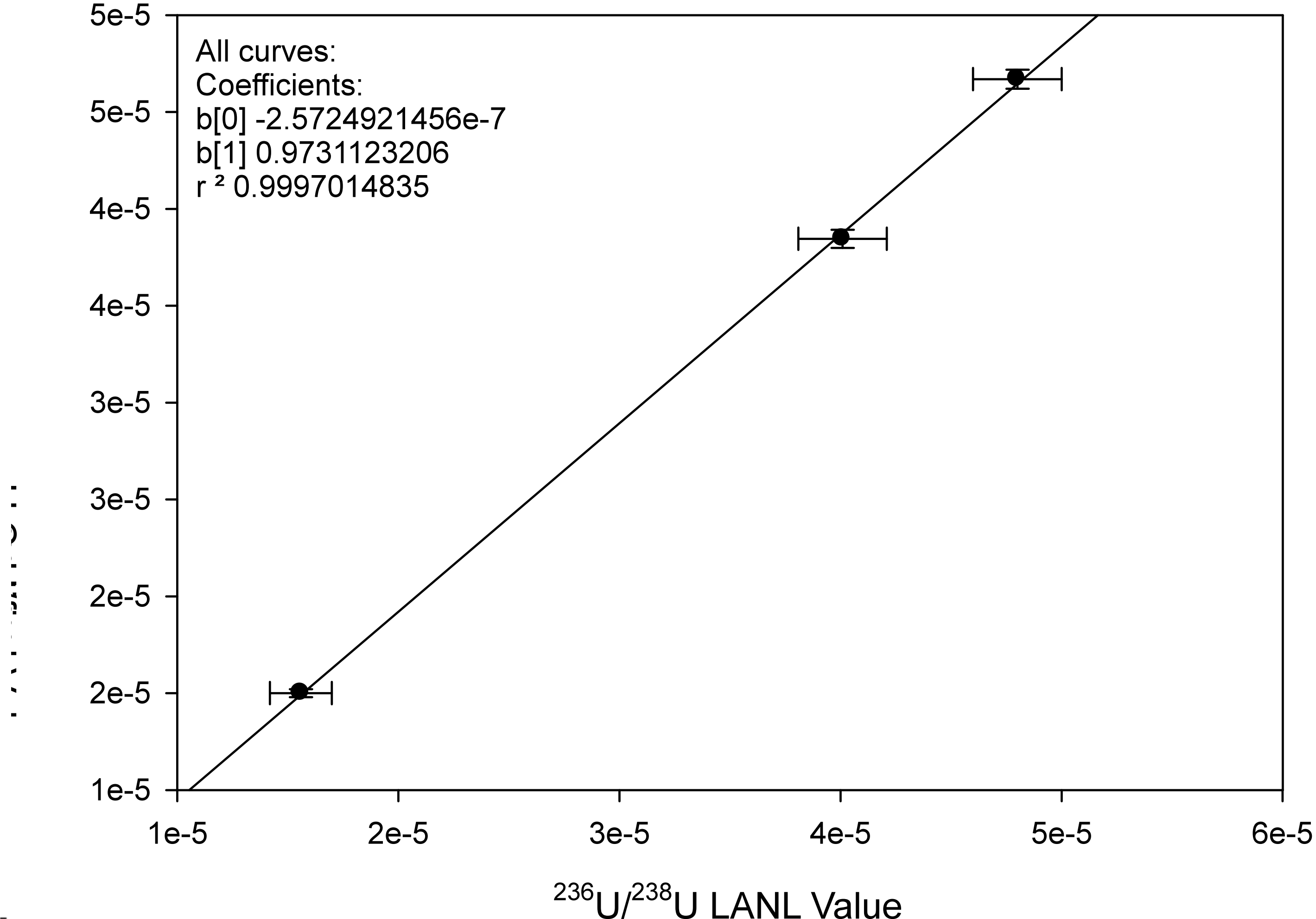
^{241}Pu / ^{239}Pu Blind QC Performance



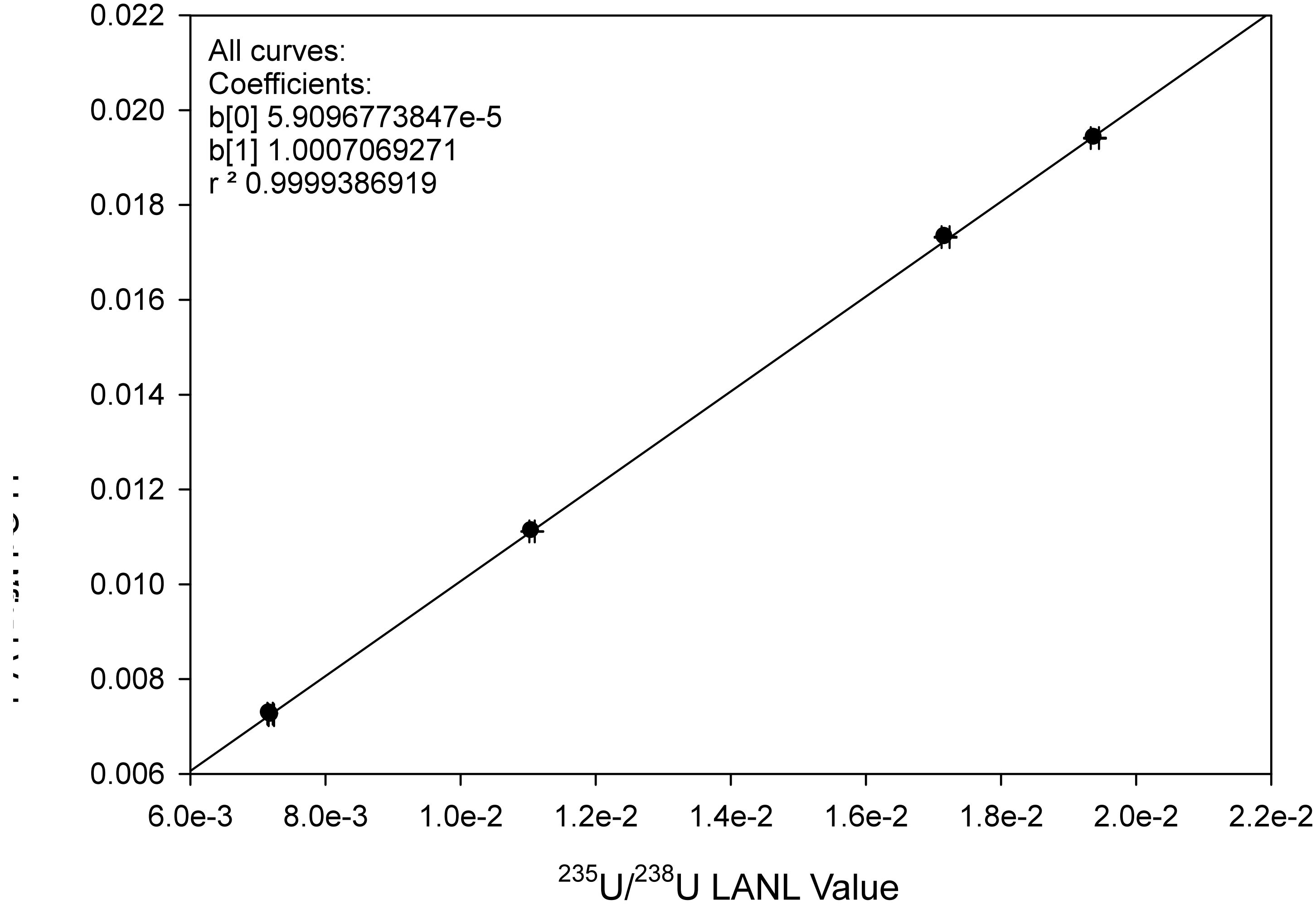
^{234}U / ^{238}U Blind QC Performance



^{236}U / ^{238}U Blind QC Performance



^{235}U / ^{238}U Blind QC Performance



NWAL Environmental Safeguards Summary

- Extremely large sample dynamic range
  - Multiple facilities and extreme care taken to prevent facility contamination and sample cross contamination
  - Screening by gamma-spec, gross alpha, and ICP-MS
- Blank must be well understood and routinely monitored for best U isotopic sensitivity
- New multi-collector TIMS capability should push down Pu detection limits, improve isotopic precision at low levels

Destructive Analysis Summary

- Destructive analysis methods are the benchmark methods for high-precision SNM assay and isotopic measurements
  - Titration methods for traditional safeguards / accountability
  - TIMS / ICP-MS for isotopic analysis
  - IDMS for environmental safeguards

- Quality Assurance is essential for successful DA program
  - Facility considerations
  - Blank control
  - Blind QC exchanges